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SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS

II. PROPYNE-3-d_3 AND PROPYNE-d_4[1]

BY L. C. LEITCH AND R. RENAUD

ABSTRACT

A procedure for preparing magnesium carbide, Mg_2C_3, in 300 gm. lots is described. Propyne-d_4 was prepared in good yields by the action of deuterium oxide on this carbide. The acetylenic deuterium in propyne-d_4 was replaced by hydrogen via the mercury derivative giving propyne-3-d_3. The vapor pressures of propyne-3-d_3 and propyne-d_4 were determined between −25°C. and −60°C.

INTRODUCTION

Since the discovery of deuterium, organic compounds which are completely deuterated or contain deuterium atoms in specific positions in the molecule have been extremely useful in interpreting molecular spectra, particularly in the infrared region (3). In view of the interest in propyne-3-d_3 and propyne-d_4 in this connection, it was decided to undertake their synthesis. Furthermore, these deuterated compounds would serve as useful starting materials for the synthesis of others.

Although propyne is most conveniently prepared by the alkylation of sodium acetylide (9), this method could not be used for the synthesis of propyne-3-d_3 because the methyl halides containing deuterium were not readily accessible. The preparation of propyne-d_4 by this method was even less practical since a large amount of deuterated ammonia would be required as a solvent. The dehydrobromination of 1,2-dibromopropane was also dismissed because the corresponding deuterated compound was not available. Besides, this reaction is known to give propyne contaminated with a certain amount of allene (5).

It appeared probable that propyne-d_4 would be obtained in good yields by the action of deuterium oxide on a carbide of magnesium, Mg_2C_3, which was discovered by Novak (7) and shown by him to evolve solely propyne when decomposed by water. Irmann (6) repeated the work of Novak and set forth the optimum conditions for the preparation of this carbide. During the last war it was investigated in Germany as a source of propyne for the synthesis of methallyl polymers (2). However, information on the process is meager. While our work was in progress, a paper appeared (8) which confirmed the results previously reported by Novak and by Irmann. The carbide was generally prepared in small amounts by passing a hydrocarbon vapor, suitably pentane or ethylene, over a few grams of finely divided magnesium in a tube

[1] *Manuscript received in original form January 19, 1951, and, as revised, November 16, 1951.*

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heated to 700 ± 25°C. Since several moles of propyne-d_4 were eventually required in the present work, a procedure was developed which gave about three hundred grams of the carbide at a time. This material consisted of a mixture of the desired carbide, unreacted magnesium, and free carbon, but only traces of the normal carbide, MgC_2.

When a suspension of this carbide in anhydrous dioxane was treated with deuterium oxide, an excellent yield of propyne-d_4 was obtained. The crude product was freed of traces of acetylene and further purified by conversion into the mercury derivative. Pure propyne-d_4 was regenerated from the dipropynyl mercury by hydrolysis with deuterated reagents. The mass spectrum of this material indicated it contained 93.3 mole % propyne-d_4 and 6.5 mole % propyne-d_3. Its infrared absorption spectrum showed a strong band in the region of 1000 to 1150 cm.$^{-1}$ due to the bending vibrations of the deuteromethyl group. The band in the region of 2548 cm.$^{-1}$ attributed to the stretching vibrations of the acetylenic deuterium group was also present.

TABLE I

VAPOR PRESSURES (P) OF PROPYNE-3-d_3 AND PROPYNE-d_4

$CD_3.C{:}\,CH$		$CD_3.C{:}\,CD$	
Temp., °C.	P, cm.	Temp., °C.	P, cm.
−24.0	75.40	−24.8	73.80
33.0	49.80	27.2	66.34
37.7	39.80	38.3	39.20
42.0	31.80	44.3	29.10
46.5	25.20	49.7	22.00
52.8	17.95	55.5	16.12
58.0	13.40	63.0	10.50
63.5	9.45		

Hydrolysis of dipropynyl mercury in 6 N hydrochloric acid yielded propyne-3-d_3. The purified product analyzed 98 mole % propyne-d_3, by mass spectrometry. Its infrared absorption spectrum showed the strong band in the region of 1000 to 1150 cm.$^{-1}$ due to the deuteromethyl group observed in the spectrum of propyne-d_4 but the band at 2548 cm.$^{-1}$ due to the acetylenic deuterium group was absent.

The vapor pressures of the deuterated propynes were determined between −25°C. and −64°C. in an apparatus similar to that described by Booth and Swinehart (1). The values obtained for each compound are listed in Table I and plotted logarithmically in Fig. 1. The line representing the vapor pressure of ordinary propyne was plotted from the data reported by Heisig and Hurd (4).

The synthesis of other compounds from propyne-d_4 is being continued and will be reported later.

EXPERIMENTAL

Magnesium Carbide, Mg_2C_3

The reaction was carried out in the apparatus shown in Fig. 2. A stainless steel tube, 2 in. in diameter and 36 in. in length, with an inlet tube $\frac{1}{4}$ in. in

diameter welded on at one end was filled with 200 gm. of fine magnesium powder. The reactor was closed with a screw cap to which a concentric thermometer well C, 30 in. in length, and an outlet tube were welded. Pentane was stored in funnel A and added as required to the tube B which was immersed in a water bath at 35°C. The apparatus was swept out with a current of dry

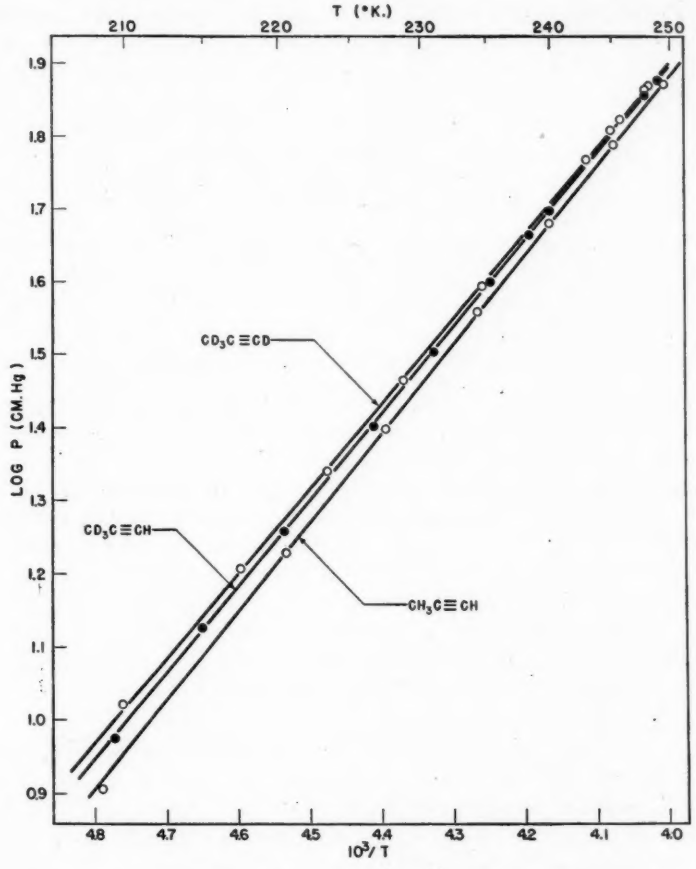

FIG. 1. Vapor pressure of propyne-d_4, propyne-3-d_3, and propyne.

argon while the temperature of the reactor was raised to 630°C. A stream of pentane vapor was then passed over the magnesium at the rate of 0.5 mole per hour until a total of 300 gm. had been used. The reactor was then cooled while a slow current of argon was passed into the apparatus. The yield of crude carbide which was removed by ramming the reactor with a steel bar was 290 to 317 gm. It analyzed 76% magnesium carbide.

Propyne-d_4, $CD_3.C{:}CD$

Crude magnesium carbide (40.0 gm.) was placed in a half liter three-necked round-bottomed flask fitted with a dropping funnel, an inlet tube for introducing argon, a stirrer with a mercury seal, and a short, jacketed Vigreux column. A spiral trap cooled to −78°C. by means of acetone and dry ice was attached to the sidearm of the column. The carbide was moistened with dioxane (10 ml.) which had been previously dried by distillation over sodium. A mixture of dry dioxane (30 ml.) and deuterium oxide (8.0 ml.; 99.7 mole %) was added dropwise with stirring over a period of two hours. The reaction mixture became

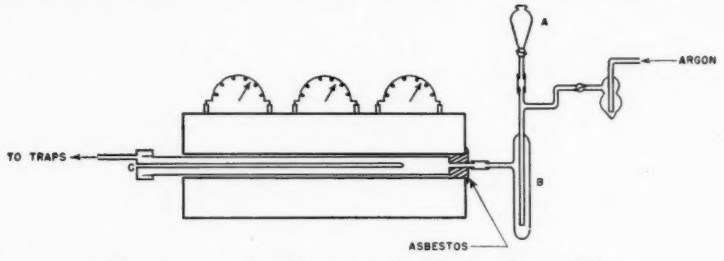

FIG. 2. Apparatus for preparation of magnesium carbide.

warm and ultimately refluxed owing to the heat of the reaction. Additional amounts of dioxane–deuterium oxide solution were added until no further evolution of heat occurred. A total of about 100 ml. of solution was generally required. The reaction mixture was finally heated under reflux for one hour while a slow current of dry argon was passed through the apparatus. The propyne-d_4 in the receiver was distilled over phosphorus pentoxide on a vacuum line. It was freed of traces of acetylene by fractional distillation from a bath at −40°C. The yield was 16.0 ml. measured at −78°C.

Unreacted deuterium oxide was recovered as a binary mixture with dioxane and reused. The deuterium oxide content was determined from its index of refraction. The yield of propyne-d_4 based on the heavy water actually consumed was over 95% of the theoretical amount.

This product is sufficiently pure for synthetic work. However, for spectroscopic purposes and vapor pressure determination it was further purified through the mercury derivative as described below.

A trap containing 10-15 ml. of liquid propyne-d_4 on a vacuum line was frozen with liquid nitrogen. The line was evacuated and the propyne was allowed to melt and evaporate slowly into a flask containing alkaline potassium mercuric iodide solution (150 ml.) which was continuously agitated by hand. Nearly all the liquid in the trap was converted into the insoluble white mercury derivative. Owing to the obnoxious and persistent odor of dipropynyl mercury, further operations at this point were carried out in the fume cupboard. Contact with the mercurial was avoided by wearing rubber gloves. The precipitate was filtered off, washed several times with water and finally with acetone. It was purified by continuous extraction in a Soxhlet apparatus with acetone from

which it separated in white, lustrous needles, m.p. 202° to 204°C. The yield was nearly quantitative. Calc. for C_6D_6Hg: Hg, 70.13%. Found: Hg, 70.05%. Ordinary propyne gave a mercury derivative which analyzed as follows: Hg, 71.95%. Calc. for C_6H_6Hg: Hg, 72.00%.

Pure propyne-d_4 was regenerated from the dipropynyl mercury by hydrolysis with a solution of deuterium bromide in deuterium oxide. The solution was prepared by adding deuterium oxide (3.0 ml.) to a slight excess of phosphorus tribromide in a U-tube leading to a spiral trap cooled to −40°C. and a receiver containing deuterium oxide (25.0 ml.). The acid was added dropwise to dipropynyl mercury (11.2 gm.) in an apparatus similar to that which was used for decomposing the carbide. The propyne-d_4 was condensed in a trap and redistilled over phosphorus pentoxide on a vacuum line. The yield was 3.9 ml. measured at −78°C. (81.9% of the theoretical amount).

Propyne-3-d_3, $CD_3.C{:}CH$

To dipropynyl-d_3 mercury (20.0 gm.) in an apparatus similar to that which was used to decompose the carbide, 120 ml. of 6 *N* hydrochloric acid was added dropwise. The propyne-3-d_3 evolved was condensed in a receiver cooled to −78°C. When all the solid had been decomposed, the propyne which remained in the apparatus was swept out with a current of dry argon. The product was purified by distillation over phosphorus pentoxide on a vacuum line. The yield was 6.2 ml. measured at −78°C. (78% of the theoretical amount).

ACKNOWLEDGMENTS

The authors are indebted to Dr. F. P. Lossing who supplied the mass spectrometry analyses and to Mr. P. Patry who analyzed the mercury derivatives.

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DIELECTRIC DISPERSION IN SOLID POLYVINYL BUTYRAL[1]

By B. L. Funt

ABSTRACT

Dielectric dispersion in solid polyvinyl butyral was investigated at frequencies of 0.3, 1, 3, 10, 30, and 100 kc. at temperatures from 20° to 140°C. The data indicated severely restricted dipole rotation and yielded an extrapolated relaxation time of 10^4 sec. at 25°C. The application of the theory of absolute reaction rates yielded an enthalpy of dielectric relaxation of 65.2 kcal. and a constant entropy of 139 e.u. These values furnish a basis for a quantitative measure of dipole hindrance and were compared with data available for other polymers.

INTRODUCTION

Fuoss and his co-workers have performed an intensive investigation of dielectric dispersion in solid polymers (5, 6, 7, 9). Their work has shown that a semiempirical correlation between mechanical and physical properties of vinyl polymers and dielectric dispersion measurements can be obtained. Tuckett (13), Boyer and Spencer (1), and Kauzmann (8) have recently reviewed the relationships between such properties as brittle points and second order transitions, and dielectric dispersion.

The dielectric behavior of solid polymers shows marked discrepancies from the quantitative predictions of the Debye theory (8). These deviations are to be expected when the complex character of the polymer system is considered in terms of the simplifying assumptions of the original theory. The application of the theory of absolute reaction rates circumvents many of the limitations of the Debye theory and allows a quantitative comparison of the dielectric behavior of various polymers to be made (8, 10, 13).

It is convenient to characterize the effective dielectric constant ϵ^* in terms of its vector components by the relation

$$\epsilon^* = \epsilon' - j\epsilon''$$

where ϵ' is the capacitative component or usual dielectric constant, and ϵ'' is the resistive component or loss factor.

The loss factor is markedly dependent on frequency and temperature. The frequency at which the loss factor at a given temperature has a maximum may be used to define a temperature dependent relaxation time

$$\tau = \frac{1}{\omega_{max}} = \frac{1}{2\pi f_{max}} \tag{1}$$

where ω_{max} is the angular frequency of maximum absorption.

It is a well known experimental fact that $\log \tau$ is an approximately linear function of the reciprocal of the absolute temperature. This naturally suggests an energy term which Eyring succinctly expresses in the form (10)

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\frac{\Delta F^*}{RT}} \tag{2}$$

[1] *Manuscript received September 10, 1951.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.

where k and h are Boltzmann's and Planck's constants respectively, and ΔF^* is the free energy of dielectric relaxation. This can be rewritten as

$$\frac{1}{\tau} = \frac{kT}{h} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \tag{3}$$

where ΔH^* and ΔS^* are the corresponding enthalpies and entropies for dielectric relaxation.

The existing data on solid polymers indicate that these derived quantities can be used to characterize polymers (13). The major difficulty appears to be the lack of sufficient experimental data of the proper type for adequate comparisons to be made (11).

EXPERIMENTAL

Apparatus

A General Radio, model 716C, Schering type, capacitance bridge was used for the electrical measurements. The bridge was energized by a Hewlett–Packard oscillator, which was continuously variable from 20 cycles to 200

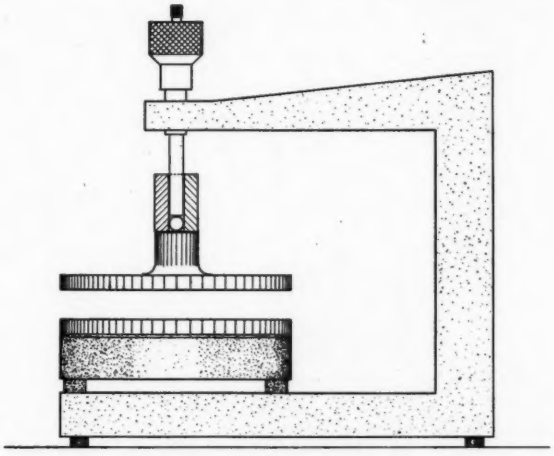


Fig. 1. Test condenser.

kilocycles. Bridge balance was determined by observing the amplified signal fed from the bridge to an oscilloscope.

The polymer samples were measured in a parallel plate condenser shown in Fig. 1. This test condenser consisted of two plane circular plates, 4.000 in. in diameter, machined from brass, and silver-plated. The lower, high potential, electrode was supported on a "micalex" support, 1 in. in thickness, which in turn rested on a rigid stand. The upper plate was fitted with a cylindrical collar. A precision micrometer head mounted on the supporting stand could be adjusted to slide into the collar and touch a steel ball resting in it. When a disk of polymer was inserted between the plates its thickness could be read *in*

situ on the micrometer. The micrometer plunger closely fitted the cylindrical collar and thus also served to center the top plate with respect to the lower one.

Samples of the polymer were pressed in a 5 in. diameter closed die for 10 min. at 160°C., and a hydraulic pressure of 16,000 lb. The resultant disks, approximately 0.05 in. thick were checked for uniformity with a micrometer. The samples were transparent and the absence of voids or air bubbles was visually evident. The disks were cut to the necessary diameter and then coated with a diluted carbon black suspension (aquadag). This coating was necessary to eliminate the air film which can cause spurious effects (5).

Previous workers have suggested various experimental techniques for overcoming this contact effect, and the "edge effect", due to the nonuniform electric

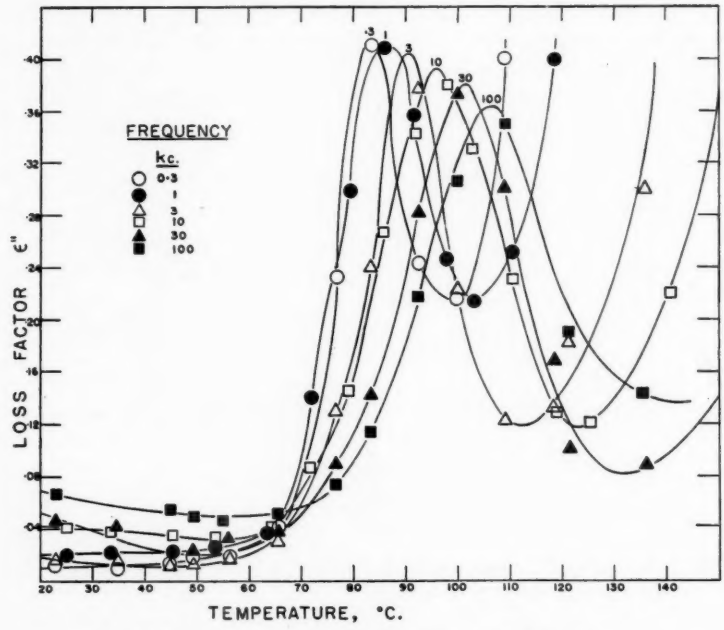


Fig. 2. Effect of frequency and temperature on loss factor.

field at the boundaries of the sample (2, 5). Coated samples with a guard ring inscribed on one side were found to yield unreliable results owing to occasional flaking of graphite at high temperatures. In the present investigation it was found that samples coated with graphite on both sides gave the most satisfactory results. The absence of a guard ring resulted in small errors for which corrections were available (12).

The condenser was calibrated by inserting sets of small spacers between the plates, measuring the capacitance, and extrapolating to infinite thickness to obtain the stray capacitance. The geometric capacitance was obtainable from

the slope of this curve and agreed with standard formulae for the capacitance of parallel circular plates.

Materials

A sample of polyvinyl butyral resin XYSG (high molecular weight) was supplied by Canadian Resins and Chemicals Co. The approximate composition was stated to be: vinyl: 54.4%, butyraldehyde: 38.3%, acetate: 0.3%, hydroxyl: 7.0%. The specific gravity was 1.12 and $[\eta] = 1.16$ in cyclohexanone at 20°C. The samples were dried *in vacuo* for 24 hr. before being pressed into disks.

The temperature of the cell and samples was automatically controlled within 0.1° in a circulating air oven.

RESULTS AND DISCUSSION

The results of measurements performed at frequencies of 0.3, 1, 3, 10, 30, and 100 kilocycles at temperatures from 25 to 140°C. are shown in Figs. 2 and 3. The interpolated data from the experimental curves are given in Table I.

It is evident that these measurements are in qualitative agreement with the Debye theory (3). Dispersion maxima in the loss factors are shown in Fig. 2,

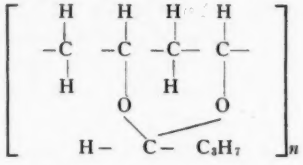
TABLE I

DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL BUTYRAL

Temp., °C.	Frequency, kilocycles					
	0.3	1	3	10	30	100
(*a*) *Dielectric constants*						
30	3.17	3.15	3.15	3.15	3.15	3.15
40	3.25	3.23	3.23	3.23	3.23	3.20
50	3.35	3.33	3.30	3.30	3.30	3.28
60	3.47	3.45	3.43	3.38	3.35	3.30
70	3.83	3.75	3.67	3.60	3.60	3.50
80	4.88	4.52	4.18	4.00	3.88	3.75
85	5.54	5.05	4.52	4.24	4.10	3.93
90	5.88	5.58	5.03	4.54	4.30	4.10
95	6.08	5.83	5.57	4.92	4.60	4.31
100	6.12	5.97	5.37	5.35	5.05	4.60
110	6.10	6.00	5.87	5.63	5.45	5.08
120	6.00	5.87	5.67	5.55	5.50	5.35
(*b*) *Loss factors*						
30	.012	.021	.016	.040	.040	.061
40	.012	.024	.012	.026	.026	.054
50	.014	.024	.012	.026	.024	.050
60	.028	.030	.020	.032	.028	.049
70	.080	.092	.060	.070	.052	.056
80	.364	.328	.172	.160	.112	.090
85	.404	.408	.270	.240	.160	.128
90	.276	.392	.403	.329	.230	.180
95	.228	.284	.328	.392	.318	.254
100	.216	.230	.220	.362	.374	.316
110	.408	.250	.122	.238	.284	.340
120	....	....	.194	.124	.132	.220

and it can be seen that these maxima are shifted to higher temperatures with increasing frequency. Similarly the usual sigmoid shape curves for dielectric constant are evident in Fig. 3.

From the structure of the polymer unit



it was expected that dipole rotation would be severely restricted. Since the relatively polar side group is attached to the main polymer chain at two points,

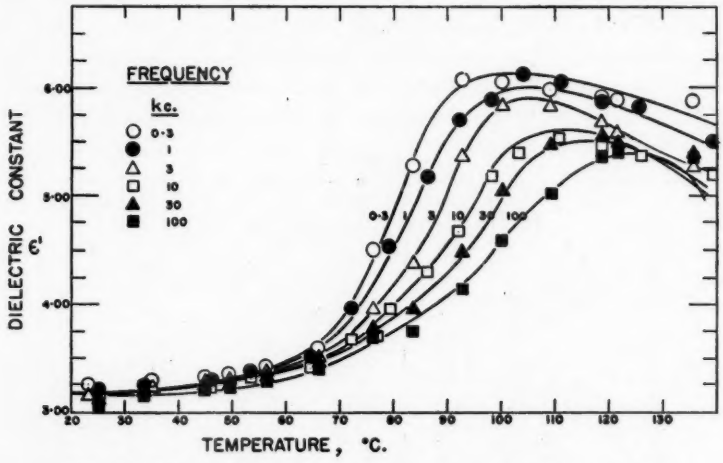


Fig. 3. Effect of frequency and temperature on dielectric constant.

the freedom of rotation about the carbon–oxygen bonds should be small. This structural restriction should be evidenced in a comparison of the electrical properties of polyvinyl butyral with those of polyvinyl acetate. In the latter polymer the polar side group is attached to the repeating polymer unit at a single point.

From the results it can be seen that the dispersion in polyvinyl butyral occurs at relatively high temperature at low frequencies. As expected the dispersion maxima were found at a higher temperature at the same frequency than for the corresponding esters such as polyvinyl acetate (9) where there is a greater freedom for rotation about the carbon oxygen bond. More quantitative methods of comparison will be considered below.

A closer examination of the data shows discrepancies from the Debye theory: (1) the maxima in Fig. 2 are about $\frac{1}{4}$ of the value $\frac{1}{2}(\epsilon_s - \epsilon_0)$ predicted by the

Debye theory (where ϵ_s is the value at low frequency and ϵ_0 the value at very high frequency); (2) the loss factor curves are not symmetrical about their maxima and show a second frequency dependent increase at higher temperatures; (3) the slopes of the dielectric constant curves decrease with increasing frequency.

The first two of these deviations are commonly found in studies of solid polymers. They can be attributed to a distribution of relaxation times in the polymer in contrast with the single relaxation time demanded by the Debye theory.

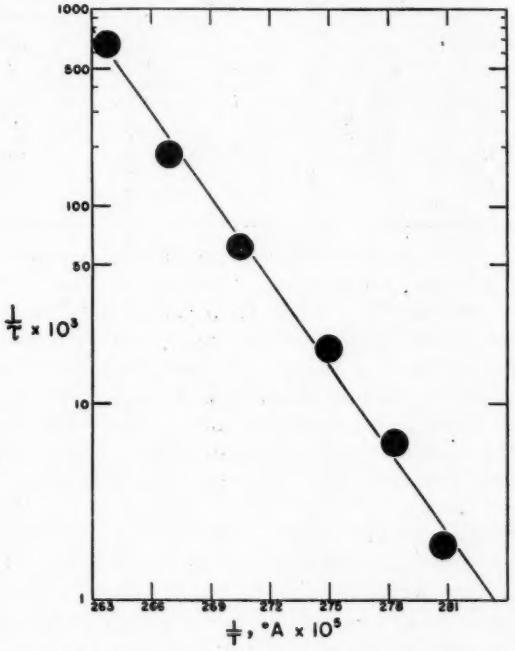


Fig. 4. Logarithmic plot of relaxation time against reciprocal of absolute temperature.

The maxima of the loss factor curves determined directly from Fig. 2 were converted into relaxation times by Equation (1). The values of the relaxation times thus obtained were plotted against the reciprocal of the absolute temperature. The result is shown in Fig. 4 where it can be seen that a straight line was obtained. Extrapolation of this line to a relaxation time of one second yielded a temperature of 72°C. for the loss factor maximum. Since this is the approximate time of a brittle point test this temperature can be compared with the brittle temperature of the polymer (11, 13). Extrapolation of Fig. 4 to 25°C. yielded a relaxation time of 10^4 sec. This high value is another quantitative indication of the restricted freedom of dipole movement in this polymer.

Since the dependence of log τ on the reciprocal temperature is linear, the slope of this line defines an energy. This energy is conveniently expressed in terms of the theory of absolute rates by Equations (2) and (3).

Values of ΔF^* were obtained from Equation (2) and of ΔH^* from the slope of Fig. 4 and Equation (3), and of ΔS^* by subtraction. The results of these calculations are tabulated in Table II.

TABLE II

EVALUATION OF ENTHALPY, ENTROPY, AND FREE ENERGY OF DIPOLE ROTATION

f_{max}, kc.	T_{max} °A.	ΔF^*, kcal.	ΔH^*, kcal.	ΔS^*, e.u.
0.3	356.1	15.7	65.2	139
1	359.2	15.2	"	139
3	363.6	14.4	"	140
10	369.6	13.7	"	139
30	374.6	13.1	"	139
100	379.1	12.4	"	139

The constancy of the entropy values is striking, and does not appear to have been found in previous investigations. The large entropy of 139 e.u. can be compared with the values 263 found for polyvinyl chloride (8), and 122 for polyvinyl acetate (8, 9). It indicates that dipole rotation is severely restricted and that approximately 10 monomer units must be rotating together (8, 10). The enthalpy, ΔH^*, is almost identical with the energy of activation for dipole rotation. The latter is conventionally obtained from the temperature coefficient of the relaxation time. Although a linear relationship between the logarithm of the relaxation time and the reciprocal absolute temperature is usually obtained, a slight curvature would be expected from Equation 2. The high value of 65.2 kcal. is of a different order of magnitude from that recently found by us for concentrated solutions of polyvinyl acetate (4). It compares reasonably, however, with the value 57.3 kcal. reported for solid polyvinyl acetate (8). The high value again reflects the severely restricted movement in the chains of the polyvinyl butyral polymer.

The sharp increase at high temperatures in the loss factors shown in Fig. 2 deserves further comment. It should be noted that the loss factor is almost independent of dimensional changes. Strictly the tangent of the phase angle, tan δ, is independent of dimensional changes. It is therefore necessary to explain the increases in loss factor on some logical basis and not attribute them to spurious dimensional changes at high temperatures. Fuoss (6) has attempted an explanation of somewhat similar data on the basis of ionic conductance, but such an explanation is not completely satisfactory. The possibility of a second dispersion maximum near the softening point of the polymer cannot be disregarded in the present work. It was not possible to resolve this point, however, since higher temperatures could not be employed without incurring the danger of deforming or decomposing the sample.

ACKNOWLEDGMENT

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THE PAPILIONACEOUS ALKALOIDS

XV. THE STRUCTURE AND THE PARTIAL SYNTHESIS OF RHOMBIFOLINE[1]

By William F. Cockburn[2] and Léo Marion

ABSTRACT

Rhombifoline is isomeric with thermopsine and anagyrine, and, like both these alkaloids, contains an α-pyridone ring. It can be dealkylated to cytisine, and, on catalytic hydrogenation, yields octahydrodesoxyrhombifoline, which is identical with hexahydrodesoxy-N-(*n*-butyl)-cytisine, the hydrogenation product of N-(*n*-butyl)-cytisine. The results of the hydrogenation thus indicate that the molecule of rhombifoline contains a third double bond, which is shown by its infrared spectrum to be located at a terminal methylene group. Rhombifoline is therefore N-(but-3-enyl)-cytisine, a conclusion which was confirmed by the partial synthesis of the alkaloid from cytisine.

Rhombifoline occurs in *Thermopsis rhombifolia* (Nutt.) Richards along with 3-methoxypyridine, cytisine, N-methylcytisine, *l*-thermopsine, and anagyrine (6). Its formula was originally reported as $C_{15}H_{20}O_2N_2$, but reanalysis of its derivatives now shows that this should be corrected to $C_{15}H_{20}ON_2$, making the alkaloid isomeric with thermopsine and anagyrine. Like the latter, rhombifoline distilled as a thick, almost colorless oil, which failed, however, to give consistent results on repeated analysis. The above formula was derived from numerous analyses of the hydrochloride, perchlorate, picrate, and chloroplatinate. The homogeneity of the base was tested by chromatography, but no separation was achieved. It is apparently susceptible to air oxidation, however, since a sample of the base which has been allowed to stand in air several days darkens in color, and does not readily form a perchlorate.

Although there are two nitrogen atoms in the molecule, rhombifoline behaves as a monoacidic base towards most salt-forming acids; potentiometric titration of the perchlorate with sodium hydroxide solution shows only one inflection in the neutralization curve, giving a pK value of 7, and a molecular weight of 325 for the perchlorate. In addition, the single oxygen atom is neutral, exhibiting neither ketonic nor hydroxylic reactions, which suggests that it is combined with the neutral nitrogen atom in a lactam grouping. This is confirmed by the infrared spectrum of a chloroform solution of the base, which shows a strong carbonyl peak at 1651 cm.$^{-1}$, with smaller peaks at 1565 and 1552 cm.$^{-1}$, which is typical of α-pyridones (7, 1) and no band in the NH and OH region (Fig. 1). The presence of an α-pyridone ring is further confirmed by examination of the infrared spectrum of the product obtained by hydrogenation of the alkaloid with Adams' catalyst in glacial acetic acid, which shows only a carbonyl peak at 1611 cm.$^{-1}$, typical of α-piperidones (7, 1). The fact that rhombifoline gives a red-brown color with aqueous ferric chloride also indicates the presence of such a ring.

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[2] *National Research Council of Canada Postdoctorate Fellow (1949-1951).*

A preliminary examination of rhombifoline by chemical methods gave little information as to the structure of the remainder of the molecule. With bromine in carbon tetrachloride, a solid perbromide was formed, which gradually evolved bromine on standing, leaving a red gum which could not be purified. No reaction was obtained with acetic anhydride in the presence of either sulphuric acid or pyridine, the alkaloid being recovered unchanged. A similar result was obtained by refluxing with alkaline ferricyanide solution. With neutral permanganate in acetone, however, after an initial period of sluggish

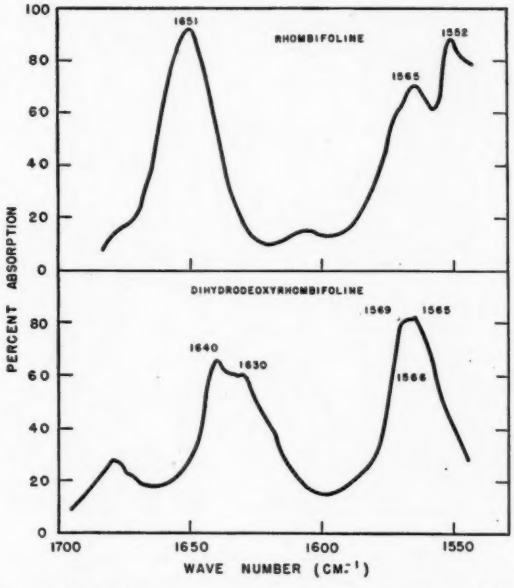


Fig. 1. Infrared spectra of chloroform solutions of the bases, using a calcium fluoride prism. Concentration of rhombifoline 3 mgm. per ml. Concentration of dihydrodesoxyrhombifoline 10 mgm. per ml.

reaction, extensive oxidation took place, and no identifiable products were isolated. Attempts to form a methiodide by heating with methyl iodide in methanol solution in a sealed tube yielded only the hydriodide of the base, while milder methods gave unchanged starting material.

Hydrogenation with Adams' catalyst in 2*N* hydrochloric acid, a method first used by Galinovsky for the conversion of α-pyridone and α-piperidone bases to the fully saturated form (3), gave an uptake of five molecules of hydrogen. The product was a mobile, pale-yellow oil, b.p. 140-145° at 14 mm., which readily formed a monoperchlorate, m.p. 139-140°. Since saturation of the pyridone ring only accounts for four molecules of hydrogen, the presence of a third double bond in the molecule is indicated. This was confirmed by analysis of the reduced base and its perchlorate, which indicated the formula $C_{15}H_{28}N_2$, corresponding to octahydrodesoxyrhombifoline. When the hydro-

genation was carried out in glacial acetic acid, slightly more than three molecules of hydrogen were taken up, corresponding to conversion of the pyridone to a piperidone ring, and saturation of the third double bond. The product could be distilled in two fractions; the first being a mobile oil, b.p. 60-70° at 0.2 mm., which was not analyzed, but showed no carbonyl or hydroxyl band in its infrared spectrum; while the second was a more viscous oil, b.p. 70-100° at 0.2 mm., which failed to give a picrate or perchlorate, and appeared from

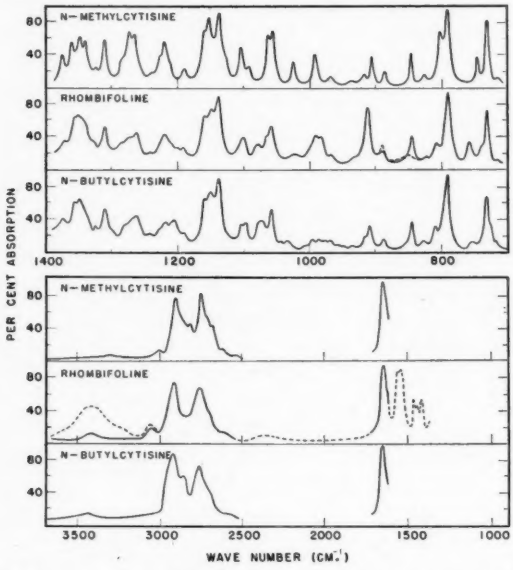


Fig. 2. Infrared spectra of carbon disulphide solutions of the bases, containing 10 mgm. per ml., and using a rock salt prism. The broken line in the spectrum of rhombifoline gives the absorption of a liquid film of the alkaloid.

the analytical figures to be a mixture.[3] The latter compound showed a band in its infrared spectrum at 1611 cm.$^{-1}$, corresponding to an α-piperidone, but it could not be purified further. In a repeat run, however, the products were separated by chromatography, the main fraction being obtained as a yellow oil which analyzed for $C_{15}H_{26}ON_2$. On further hydrogenation in 2*N* hydrochloric acid, this oily product took up another two molecules of hydrogen, yielding a colorless, mobile oil, which, however, was apparently different from octahydrodesoxyrhombifoline. The perchlorate melted diffusely at 175-190°, and yielded analytical figures indicating that it was not homogeneous.

Much more valuable information was obtained from the infrared spectrum in the "fingerprint" region. As can be seen from Fig. 2, a comparison of the spectra of rhombifoline and N-methylcytisine shows that a large proportion

[3]*Leonard and Marion report a similar result with dehydrolupanine (MA), which gave a mixture of α-isolupanine and α-isosparteine on hydrogenation with Adams' catalyst in glacial acetic acid, owing to partial reduction of the carbonyl group (5).*

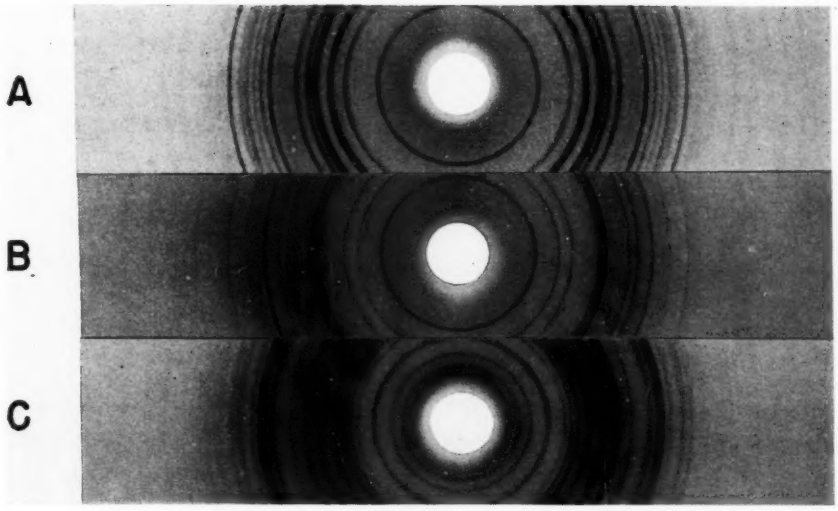


Fig. 3. X-ray powder photographs taken on a Philips camera of 114.59 mm. diameter using a Co target with Fe filter. *A*: cytisine perchlorate. *B*: Rhombifoline perchlorate. *C*: N-methylcytisine perchlorate.

of the peaks in one can be matched with corresponding peaks in the other, differing more or less in shape and intensity, but of approximately the same wave lengths. This similarity in spectra, which is even more pronounced than was noted for anagyrine and thermopsine (1), suggests a possible structural relationship, the most obvious being that of N-alkylcytisines. It was found that N-methylcytisine can be demethylated to cytisine in 50-60% yield by heating the hydriodide in the presence of ammonium iodide, under the conditions of the Herzig-Meyer N-methyl determination. Under the same conditions, rhombifoline gave a 45% yield of cytisine, proving either that it is an N-alkylcytisine, or that it is a mixture containing a large proportion of N-methylcytisine or cytisine itself. The latter possibility is ruled out by a comparison of the X-ray powder photographs of the perchlorates of cytisine, N-methylcytisine, and rhombifoline (Fig. 3). The three patterns are quite distinct, and preclude the possibility of rhombifoline containing either of the other two in anything but the most minute traces. Anagyrine, which has no free alkyl group, was recovered unchanged when submitted to the same treatment. Hence rhombifoline consists of cytisine with an N-alkyl group containing four carbon atoms and one double bond, and can be written $C_{11}H_{13}ON_2.C_4H_7$.

In order to ascertain whether the N-alkyl group is a straight or branched chain, N-*n*-butylcytisine was synthesized by refluxing equimolecular amounts of cytisine and *n*-butyl bromide in acetone in the presence of potassium carbonate. The product was a yellow oil which analyzed as $C_{15}H_{22}ON_2$, and gave a perchlorate m.p. 246-8°. The melting point was depressed to 237-9° by admixture with rhombifoline perchlorate. Hydrogenation with Adams' catalyst in 2 *N* hydrochloric acid gave hexahydrodesoxy-N-*n*-butylcytisine, which was converted directly to the monoperchlorate, m.p. 139-140°. This melting point was not depressed by admixture with octahydrodesoxyrhombifoline monoperchlorate, and the two compounds are identical. Rhombifoline is therefore an N-*n*-butenylcytisine, and it only remained to discover the position of the double bond.[4]

Below is a table, based on various sources (2, 8, 9, 10) of the probable position of the principal infrared absorption bands used to distinguish between different types of ethylenic double bond.

TABLE I

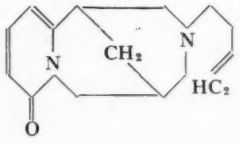
PROBABLE POSITIONS OF THE PRINCIPAL ABSORPTION BANDS ASSOCIATED WITH DIFFERENT TYPES OF ETHYLENIC BOND

$R.CH = CH_2$	$R.CH = CH.R$	$R_2C = CH_2$	$R_2C = CH.R$
910 and 990 cm.$^{-1}$	965 (*trans*)	890	810–840
1640	1670	1640	1670
3000–3100 and 2900–3000	2950–3050	3040–3120 (3080) and 2910–3040	2950–3050

[4]*The nonreactivity of this double bond towards permanganate and bromine is difficult to explain, but may be connected with the comparatively large size of the molecule.*

The carbon–carbon stretching absorption at 1640-1670 cm.$^{-1}$ shown by ethylenic double bonds is relatively weak, and would be obscured by the strong carbonyl band at 1651 cm.$^{-1}$, and an attempt was made to remove this group by reduction with lithium aluminum hydride. The spectrum of the product showed, in addition to the conjugated double bonds at 1569 and 1565 cm.$^{-1}$, a double peak at 1630-1640 cm.$^{-1}$, which may be due to a terminal methylene group (Fig. 1).[5] The analysis of this dihydrodesoxyrhombifoline was unsatisfactory, however, and more definite evidence was sought. This was found in a comparison of the infrared spectra in the "fingerprint" region (650 to 1500 cm.$^{-1}$) of rhombifoline and N-*n*-butylcytisine (Fig. 2). It can be seen that the two are very similar, except for additional bands in rhombifoline at 759, 911, 982, 990, and 3060 cm.$^{-1}$. The band at 759 cm.$^{-1}$ has often been found to occur in the spectra of other lupine alkaloids, and may or may not be present in the spectra of different samples of the same compound. It is possibly due to contamination with extracting solvent, such as chloroform, and may be discounted, while that at 990 cm.$^{-1}$ is also present in the spectrum of N-methylcytisine, and may therefore be due to a skeletal vibration. Hence the significant bands are those at 911, 982, and 3060 cm.$^{-1}$. Reference to the table above shows that these frequencies are normally given by a terminal methylene group.

Final confirmation of the structure assigned was obtained by a partial synthesis of the molecule. But-3-enol was prepared by the action of allyl magnesium bromide on trioxymethylene, and converted to but-3-enyl bromide with phosphorus tribromide in the presence of pyridine (4). The bromide was then refluxed in acetone with an equimolecular amount of cytisine in the presence of anhydrous potassium carbonate for 65 hr. The product was freed from unchanged cytisine by acetylation, and distilled as a thick yellow oil, which, on account of the behavior of natural rhombifoline, was converted directly to the picrate, perchlorate, and hydrochloride. These salts were found to have almost the same decomposition melting points as those of the corresponding salts of the natural alkaloid, and admixture caused no depression. Final proof of identity was obtained by comparison of the infrared spectra of the free bases, and X-ray powder photographs of the perchlorates, which were in both cases identical. Rhombifoline is thus N-(but-3-enyl)-cytisine, and is represented by the formula below



The close relationship of this alkaloid to thermopsine and anagyrine is obvious, and suggests that all three may stem from a common precursor.

[5]*The small band at 1680 cm.$^{-1}$ was found to increase at the expense of the 1569–1565 cm.$^{-1}$ band after the compound had been exposed to air for several hours, and may be due to an oxidation product.*

EXPERIMENTAL

All melting points are corrected, unless otherwise stated. In every case, the capillary tube was inserted in the bath or block about 15° below the melting point, with a heating rate of 3-5° per minute.

All spectra were taken on a Perkin-Elmer Model 12*c* Spectrometer, with a 1 mm. cell.

Rhombifoline

The alkaloid was obtained from *Thermopsis rhombifolia* by hot methanol extraction, and fractional vacuum distillation of the purified bases, and purified by recrystallization of the perchlorate from water until the melting point was constant at 243-245° (6). The free base distilled as a thick yellowish oil b.p. 120° at 0.2 mm. (air-bath temperature), $[\alpha]_D^{25}$ −232.4° (*c*, 2.130 in ethanol), which could be reconverted to the same perchlorate. The analysis results were inconsistent, however, and varied between the values calculated for $C_{15}H_{20}ON_2$ and $C_{15}H_{22}O_2N_2$. That this was due to partial hydration is supported by the fact that the infrared spectrum of a liquid film of the base showed a pronounced band at 3410 cm.$^{-1}$, possibly corresponding to a bonded OH (Fig. 2). This band is in the NH region also, however, and may indicate slight dealkylation on distillation, which would also account for the poor analysis figures. Consistent results were obtained with the following salts:

Hydrochloride.—A methanolic solution of the alkaloid was made just acid to Congo red by the addition of concentrated hydrochloric acid, evaporated to dryness in vacuum, and the residue recrystallized from methanol–acetone. It was obtained as nacreous white platelets, m.p. 256-258° (dec.). Calcd. for $C_{15}H_{20}ON_2.HCl$: C, 64.15; H. 7.54; N, 9.98. Found: C, 64.44, 64.32; H, 7.37, 7.53; N, 9.69%. This salt could be sublimed unchanged at 120° at 10^{-4}mm. Found: C, 64.30, 64.48; H, 7.50, 7.69%.

Perchlorate.—This was obtained by the standard procedure as colorless flat spears from water, m.p. 243-245° (dec.). Calcd. for $C_{15}H_{20}ON_2.HClO_4$: C, 52.24; H, 6.14; N, 8.13. Found: C, 52.51, 52.48, 52.49; H. 5.72, 5.99, 5.84; N, 8.03, 8.22%.

Picrate.—Formed by mixing equimolecular amounts of rhombifoline and picric acid in methanol, and recrystallization from acetone–methanol. Obtained as flat, efflorescent needles, m.p. 226° (dec.) which were dried at 60° in high vacuum for analysis. Calcd. for $C_{15}H_{20}ON_2.C_6H_3O_7N_3$: C, 53.27; H, 4.89; N, 14.79. Found: C, 53.04, 53.22; H, 4.80, 4.71; N, 14.89%.

Chloroplatinate.—Crystallized in red needles from acidified aqueous methanol, m.p. 268°. Calcd. for $C_{15}H_{20}ON_2.H_2PtCl_6$: C, 27.53; H, 3.39; Pt. 29.84. Found: C, 26.16; H, 3.52; Pt, 29.33%.

The hydriodide and hydrobromide had unsharp melting points, and appeared from the analysis figures to be variable in constitution between the mono- and di-salts.

Potentiometric Titration

An aqueous solution of 50 mgm. rhombifoline perchlorate was titrated at 20°

against 0.100 *N* sodium hydroxide solution, using a Beckmann pH meter. The single end point gave a value of pK 7 for the base, and a molecular weight of 325 for the perchlorate.

Chromatography of Rhombifoline

A freshly distilled sample of the alkaloid was chromatographed on alumina of activity I, but came through in a homogeneous band with a solvent containing equal parts by weight of chloroform and ether. This band was quantitatively converted to pure rhombifoline picrate, m.p. 226°.

Hydrogenation

(1) *Octahydrodesoxyrhombifoline*

Rhombifoline hydrochloride (278.8 mgm.) was shaken under hydrogen with 150 mgm. Adams' catalyst in 10 ml. 2 *N* hydrochloric acid. Absorption of hydrogen was slow, 10 hr. being required for completion of the reaction. The uptake corresponded to 113 ml. of hydrogen at N.T.P., while the theoretical amount for five moles is 112 ml. The solution was filtered from catalyst, alkalized with sodium hydroxide, and the free base extracted with methylene chloride. The extract was dried with potassium carbonate, the solvent removed on the steam bath, and the residue distilled in vacuum, being obtained as a mobile, light yellow oil, b.p. 140-145° at 14 mm. Calcd. for $C_{15}H_{28}N_2$: C, 76.20; H, 11.93. Found: C, 76.85; H, 11.99%. The base was converted to the perchlorate, which crystallized from methanol–ether in small colorless prisms, which melted at 139-140° without decomposition, and recrystallized on cooling. Calcd. for $C_{15}H_{28}N_2.HClO_4$: C, 53.48; H, 8.68; N, 8.32. Found: C, 53.91, 53.74; H, 8.67, 8.65; N, 8.15%.

(2) *Hexahydrorhombifoline*

Freshly distilled rhombifoline (105 mgm.) was dissolved in 20 ml. of glacial acetic acid, 100 mgm. Adams' catalyst added, and the mixture shaken under hydrogen. The solution rapidly took up 32 ml. of hydrogen (at N.T.P.) then continued to absorb gas at a much slower rate, possibly indicating slow reduction of the carbonyl group. The theoretical amount of hydrogen for three moles is 29 ml. at N.T.P. The product was freed from acetic acid in vacuum, and distilled in two fractions. The first fraction, b.p. 60-70° at 0.2 mm., was a mobile oil, which was not analyzed, but which showed no indication of CO or OH in the infrared spectrum. The second, b.p. 70-100° at 0.2 mm., was a thicker oil, the analysis of which was intermediate between the values for $C_{15}H_{26}N_2$ and $C_{15}H_{26}ON_2$. The infrared spectrum was taken in chloroform solution, using a calcium fluoride prism, and exhibited a strong band at 1611 $cm.^{-1}$ corresponding to an α-piperidone. This compound failed to give a picrate or perchlorate.

In a second run, employing 380 mgm. of free base, and the same conditions as above, the main product was purified by chromatography, being obtained as a thick yellow oil, b.p. 110-120° at 0.05 mm. Calcd. for $C_{15}H_{26}ON_2$: C, 71.94; H, 10.47. Found: C, 71.70; H, 10.47%. This compound was further hydrogenated in 2 *N* hydrochloric acid with Adams' catalyst, when it was found to take up a further two molecules of hydrogen. The product was a mobile oil,

resembling octahydrodesoxyrhombifoline in general appearance, and odor. When converted to the perchlorate, however, it was not seeded by the monoperchlorate of the latter, and when finally obtained crystalline from methanol–ethylacetate, melted diffusely at 175-190°. It was not homogeneous as shown by the analytical figures which were intermediate between those required by a monoperchlorate and those of a diperchlorate of a base $C_{15}H_{28}N_2$. Found: C, 44.46, 44.78; H, 7.69, 7.19%. The reason for this discrepancy is not known.

Dealkylation

An aqueous solution containing 206 mgm. of rhombifoline perchlorate was made alkaline with sodium hydroxide, and the free base extracted with methylene chloride. The extract was dried with potassium carbonate, and the solvent removed in vacuum. The base (145 mgm.) was placed in a 25 ml. round-bottomed flask along with 350 mgm. phenol as solvent, and heated on the steam bath to give a homogeneous melt. After cooling, 3 ml. of freshly distilled constant-boiling hydriodic acid was added, followed by 750 mgm. of ammonium iodide and five drops of 5% gold chloride solution. A strong stream of nitrogen was passed through the flask, and the temperature slowly raised to 150° and held there for 30 min. to drive off excess hydriodic acid and phenol. The temperature was then raised to 225°, and held there for five minutes, to decompose the hydriodide. After cooling, the solid residue was thoroughly triturated with hot dilute hydrochloric acid, and the acid solution filtered. The cooled solution was extracted with ether, alkalized with sodium hydroxide, and extracted again with methylene chloride. This second extract was dried with potassium carbonate, the solvent removed on the steam bath, and the residual oil distilled at 130-140° at 0.1 mm. The distillate consisted of 51 mgm. of colorless needles, m.p. 150-154°. (45% of the theoretical yield of cytisine). This was treated with an equimolecular amount of picric acid in methanol, and the picrate recrystallized from water in feathery aggregates, m.p. 286-7°. Admixture with an authentic sample of cytisine picrate caused no depression in melting point. Calcd. for $C_{11}H_{14}ON_2.C_6H_3O_7N_3$: C, 48.70; H, 4.08. Found: C, 48.75, 48.93; H, 4.22, 4.36%. The free base was liberated and sublimed, m.p. 154-6°. Admixture with authentic cytisine caused no depression. Calcd. for $C_{11}H_{14}ON_2$: C, 69.44; H, 7.42; N, 14.73. Found: C, 69.40, 69.69; H, 7.36, 7.18; N, 15.00%.

The dealkylation of N-methylcytisine and the attempted dealkylation of anagyrine were carried out under identical conditions. N-methylcytisine yielded up to 60% of cytisine, while anagyrine was recovered almost quantitatively.

N-n-butylcytisine

A solution containing 1.130 gm. of cytisine in 25 ml. acetone was stirred with 1.5 gm. of potassium carbonate under nitrogen, and 0.627 ml. (0.815 gm.) of *n*-butyl bromide added from a burette in 0.1 ml. portions every 15 min. After addition was completed, the mixture was refluxed for 20 hr. The solution was filtered, concentrated to an oil under vacuum, and 1 ml. of acetic anhydride added, followed by a few drops of pyridine. The solution was heated on the

steam bath for 15 min. to acetylate any unchanged cytisine, the mixture poured into dilute hydrochloric acid and extracted thoroughly with ether. The aqueous solution was then alkalized with sodium hydroxide, and extracted with methylene chloride. The extract was dried with potassium carbonate, the solvent removed in vacuum and the residue distilled at 140-150° at 0.2 mm. as a thick, pale yellow oil. Calcd. for $C_{15}H_{22}ON_2$: C, 73.13; H, 9.00. Found, C, 74.33, 74.13; H, 9.26, 9.46%. The perchlorate was formed in the normal way, and crystallized from methanol, m.p. 246-8°. Calcd. for $C_{15}H_{22}ON_2.HClO_4$: C, 51.93; H, 6.69; N, 8.08. Found: C, 51.98, 52.19; H, 6.50, 6.36; N, 7.97%.

Hexahydrodesoxy-N-n-butylcytisine

Freshly distilled N-*n*-butylcytisine (149 mgm.) was hydrogenated in 2*N* hydrochloric acid with Adams' catalyst. The hydrogen uptake was 55.0 ml. at N.T.P., while the theoretical volume for four molecules is 53.7 ml. at N.T.P. The solution was filtered, alkalized, and extracted with methylene chloride, and the extract dried with potassium carbonate and concentrated to an oil in vacuum. The oil was dissolved in methanol, and the solution brought to pH 7 with concentrated perchloric acid diluted with three times its own volume of methanol; the solution was concentrated on the hot plate, and seeded with octahydrodesoxyrhombifoline perchlorate. Slow crystallization ensued, and the product could be recrystallized from methanol in small prisms, m.p. 139-140°. No depression in melting point occurred on admixture with octahydrodesoxyrhombifoline perchlorate. Calcd. for $C_{15}H_{28}N_2.HClO_4$: C, 53.48; H, 8.68; N, 8.32. Found: C, 53.46, 53.60; H, 8.40, 8.64; N, 8.37%. The picrate, methiodide, and dinitrodiphenate could not be crystallized.

Dihydrodesoxyrhombifoline

Rhombifoline perchlorate (692 mgm.) was decomposed with sodium hydroxide, the free base (488 mgm.) extracted with methylene chloride and the extract concentrated to an oil, but not distilled. The oil was dissolved in anhydrous ether, and excess lithium aluminum hydride in ether added. The solution was refluxed under nitrogen for 20 hr., and the excess reagent decomposed by the cautious addition of methanol and water. The solution was filtered from aluminum hydroxide, extracted with ether, and the extract dried with sodium sulphate and concentrated to an oil in vacuum. The oil was distilled as rapidly as possible at 100° at 0.2 mm., being obtained as a yellow oil which darkened in air. Calcd. for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63. Found: C, 79.74; 79.60; H, 9.71, 9.68%. Addition of two molecules of picric acid in ether gave a flocculent orange picrate, which rapidly turned into a reddish tarry oil.

Synthetic Rhombifoline

This reaction was carried out as described for N-*n*-butylcytisine, using but-3-enyl bromide, prepared according to the method described by Juvala (4). From 1.196 gm. of cytisine, was obtained 0.950 gm. of an almost colorless oil, b.p. 120° at 0.2 mm. This was directly converted into the following salts.

Perchlorate: Colorless flat needles, m.p. 243° (dec.). Mixture with rhombifoline perchlorate melted at 243°. Calcd. for $C_{15}H_{20}ON_2.HClO_4$: C, 52.24; H, 6.14; N, 8.13. Found: C, 52.85, 52.73; H, 6.26, 6.00; N, 7.93%.

Picrate: Efflorescent flat needles, m.p. 227°. Mixture with rhombifoline picrate melted at 226°. Calcd. for $C_{15}H_{20}ON_2.C_6H_3O_7N_3$: C, 53.27; H, 4.89; N, 14.79. Found: C, 53.38, 53.10; H, 5.00, 5.01; N, 13.67%.

Hydrochloride: Nacreous plates, m.p. 258°. Mixture with rhombifoline hydrochloride melted at 258°. Calcd. for $C_{15}H_{20}ON_2.HCl$: C, 64.15; H. 7.54; N, 9.98. Found: C, 63.60, 63.43; H, 8.26, 8.16; N, 10.39%.

The free base was liberated and redistilled, and the optical rotation measured. $[\alpha]_D^{27}$ −235.8° (*c*, 6.70 in ethanol).

ACKNOWLEDGMENT

We express our gratitude to Dr. W. H. Barnes and Mrs. H. Sheppard who prepared the X-ray powder photographs; also to Dr. R. N. Jones and Mr. R. Lauzon for the infrared absorption spectra.

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THE PREPARATION OF POLYNITROETHYLENEAMINES[1]

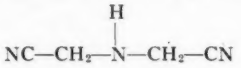
By Jean P. Picard and R. H. Meen[2]

ABSTRACT

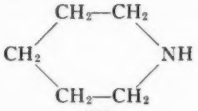
By means of chloride-catalyzed nitration, polynitroamines analogues of Edna (N,N'-dinitroethylenediamine) were prepared in fairly good yields. The compounds to be nitrated were obtained by the condensation of acetonecyanohydrin with ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. The secondary amines resulting from the condensation, although less basic in character, have nevertheless required for nitration the addition of one equivalent of chloride catalyst. When the products of the condensation with acetonecyanohydrin were isolated, as hydrochloride salts, no additional chloride was needed to assure nitration. The analysis of the hydrochloride derivatives were found to be in close agreement with the proposed structural formula.

INTRODUCTION

Formation of a nitramine by direct nitration of the amine is possible only when the amine is sufficiently weak; in other words, if the amine is a strong proton acceptor, it cannot be nitrated in satisfactory yield. Thus, a very weak basic amine such as imino-*bis*-acetonitrile (I) can be nitrated to the corresponding nitramine by an excess of acetic anhydride – nitric acid mixture, whereas a strong basic amine such as piperidine (II) requires about 5% of chloride catalyst in the nitration in order to give a good yield of nitrated product. Chute *et al.* (1) reported that a yield of only 4% of nitropiperidine was obtained when the catalyst was omitted.



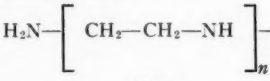
(I)



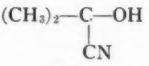
(II)

The primary amino groups at the ends of polyethyleneamine molecules (III) are strongly "proton accepting"; consequently, treatment with 100% nitric acid results in the formation of a nitrate salt which cannot be converted to the corresponding nitroamine, either by concentrated or by fuming sulphuric acid.

It appeared, therefore, that the difficulty could be overcome by converting the primary amino group into a secondary one with less basic character. This was successfully achieved by condensing acetone cyanohydrin (IV) with the primary amino group.



(III)



(IV)

From ethylenediamine, the parent substance of the polyethyleneamines, by this condensation is obtained 2,7-dicyano-2,7-dimethyl-3,6-diazaoctane (V).

[1] *Manuscript received August 21, 1951.*
Contribution from the Organic Section of the Canadian Armament Research and Development Establishment, Valcartier, Que.

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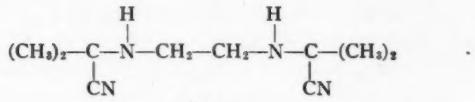

(V)

One would expect the nitrile groups of the 2,7-dicyano-2,7-dimethyl-3,6-diazaoctane decreased the proton accepting capacity of the amine so that its basicity was between that of imino-*bis*-acetonitrile (I) and that of piperidine (II). From this it was expected that (V) would nitrate to some extent without chloride catalyst, but that the addition of catalyst would increase the yield.

This behavior was confirmed by experiment. When dicyanodimethyldiazaoctane was treated with an excess of nitric – acetic anhydride mixture at room temperature for 24 hr. only 38% of the nitroamine was obtained. The yield was raised to 76% by carrying out the reaction in the presence of 4% (moles) of either acetyl chloride, hydrogen chloride, or zinc chloride. A similar behavior was observed with the higher homologues.

PREPARATION OF POLYETHYLENEAMINES

The commercial samples of polyethyleneamines were dark in color and obviously impure. Before condensation with acetonecyanohydrin, they were purified by distillation.

The condensation with ethylenediamine (b.p. 110°C.; n_D^{25} 1.4536), diethylenetriamine (b.p. 97-100°C., 20 mm.; n_D^{25} 1.4810), triethylenetriamine (b.p. 112-113°C., 1 mm.; n_D^{25} 1.4951), and tetraethylenepentamine (b.p. 151-152°C., 1 mm.; n_D^{25} 1.5015) has given the following compounds: 2,7-dicyano-2,7-dimethyl-3,6-diazaoctane (VI), 2,10-dicyano-2,10-dimethyl-3,6,9-triazaundecane (VII), 2,13-dicyano-2,13-dimethyl-3,6,9,12-tetraazatetradecane (VIII), 2,16-dicyano-2,16-dimethyl-3,6,9,12,15-pentaazaheptadecane (IX), for which the analytical data reported in Table I, are in good agreement with the following general structure.

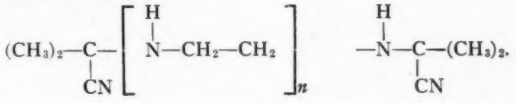

TABLE I

THE CONDENSATION PRODUCTS OF POLYETHYLENEAMINES WITH ACETONECYANOHYDRIN

No.	Empirical formula	M.p.,* °C.	Analyses, %						Yield %
			Carbon		Nitrogen		HCl		
			Calc.	Found	Calc.	Found	Calc.	Found	
VI	$C_{10}H_{18}N_4$	54.5–56	61.86	61.79	28.86	28.80			94
VII	$C_{12}H_{23}N_5.3HCl$	60–72	41.56	41.41	20.20	20.12	31.54	31.53	55
VIII	$C_{14}H_{28}N_6$	104–105	59.96	59.87	29.97	29.95			89
IX	$C_{16}H_{33}N_7.5HCl$	75–82	37.99	37.89	19.38	19.33	36.04	36.01	58

**Compounds VII and IX melting points vary with the rate of heating. Two of these compounds, VI and VIII, were obtained in a crystalline form, whilst Compounds (VII) and (IV), viscous liquids, were isolated as hydrochloride salts.*

NITRATION OF POLYETHYLENEAMINES

The ethyleneamine cyano derivatives, namely Compounds VI, VII, VIII, and IX, were converted to their corresponding nitramines by agitation with a large excess of nitric – acetic anhydride mixture at room temperature for a period of 24 hr.

The nitrating medium, even when present in large excess, did not appear to dissolve the substances. The hydrochloride salts of compounds VII and IX did not require the addition of catalyst, but the two others, VI and VIII, gave satisfactory nitration yields only in the presence of one equivalent of acetyl chloride.

Upon drowning in ice water a yellow amorphous mass precipitated out which, after a single recrystallization from nitromethane–ether mixture gave beautiful white needles (Table II).

TABLE II

NITRATION PRODUCTS OF POLYETHYLENEAMINES

No.	Empirical formula	M.p.,* °C.	Nitrogen		Yield, %
			Calc.	Found	
X	$C_{10}H_{16}N_6O_4$	212–212.5	29.56	29.47	60
XI	$C_{12}H_{20}N_8O_6$	162.5–163	30.09	30.10	70
XII	$C_{14}H_{24}N_{10}O_8$	200–200.5	30.42	30.47	65
XIII	$C_{16}H_{28}N_{12}O_{10}$	171–172	30.64	30.51	67

**All melting points corrected against reliable standards.*

The ultraviolet absorption spectrum for Compounds X and XI have shown a maximum between 235 and 240 mμ (Fig. 1). This is a well-established char-

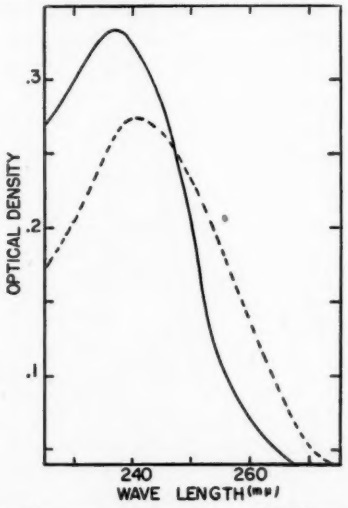

FIG. 1. Ultraviolet absorption spectra. ———— 2,7-Dicyano-2,7,dimethyl-3,6-dinitro-3,6-diazaoctane (X). Ethanol. - - - - - 2,10-Dicyano-2,10-dimethyl-3,6,9-trinitro-3,6,9-triazaundecane (XI). Ethanol.

acteristic for secondary nitroamine group (2). The high insolubility of Compounds XII and XIII in 95% ethanol or isooctane did not allow their absorption spectrum to be determined.

EXPERIMENTAL*

2,7-Dicyano-2,7-dimethyl-2,6-diazaoctane (VI); and 2,13-Dicyano-2,13-dimethyl-3,6,9,12-tetraazatetradecane (VIII)

The redistilled anhydrous ethylenediamine, 49.5 gm. (0.25 mole), was added, with stirring, to 50 cc. (0.53 mole) of acetone cyanohydrin (97%) over a period of 30 min. In order to prevent the decomposition of acetonecyanohydrin, the temperature was kept below 60°C. by a cold water bath. On cooling to 0°C. the reaction mixture changed into a crystalline mass containing a small amount of viscous oil. After removing most of the oil, by filtering with suction, the mass was washed with *n*-butyl ether. The yield was 50 gm. of soft yellow crystals. The product was recrystallized from 25 cc. of hot *n*-butyl ether and filtered at 0°C. to yield 45 gm. (or 94% of theory) of dicyanodimethyldiazaoctane (VI), m.p. 54.5-56°C. The compound was very soluble in most ordinary solvents except those such as petroleum ether and *n*-butyl ether in which it was only slightly soluble. Calc. for $C_{10}H_{18}N_4$: C, 61.86%; N, 28.86. Found C, 61.79%; N, 28.80.

Following the same procedure when freshly distilled tetramethylenetetramine (152°C. at 0.22 mm.) was used, the precipitated material obtained upon cooling to 0°C. was a white crystalline solid. This precipitate melted at 104-105°C. and was identified as 2,13-dicyano-2,13-dimethyl-3,6,9,12-tetraazatetradecane (VIII). Calc. for $C_{14}H_{28}N_6$: C, 59.96%; N, 29.97%. Found C, 59.87%; N, 29.95%.

2,10-Dicyano-2,10-dimethyl-3,6,9-triazaundecanetrihydrochloride (VII); and 2,16-Dicyano-2,16-dimethyl-3,6,9,12,15-pentaazaheptadecane Pentahydrochloride (IX)

In a closed three-necked flask containing 60 cc. (0.66 mole) of acetonecyanohydrin was added 30 cc. (0.28 mole) of anhydrous diethylenetriamine. The temperature was maintained at 40 to 50°C. by a cold water bath. After a further 45 min. stirring at room temperature, the viscous reaction was dissolved in about 500 cc. of fairly dry ether. This solution was then dried by shaking overnight over about 200 gm. of finely ground Drierite in a closed flask. The dried solution was filtered by suction.

The flask containing the filtrate was fitted with a mercury-sealed mechanical stirrer, and cooled with an ice bath. Dry hydrogen chloride was then added over a period of 20 min. The precipitated salt was filtered, washed with fairly dry ether, and dried overnight under vacuum at room temperature. The yield was usually about 54 gm. or 55% of theory.

The salt obtained from three separate batches was prepared and analyzed for hydrogen chloride by silver nitrate precipitation. Calc. for $C_{12}H_{23}N_5.3HCl$

**All melting points corrected against reliable standards.*

(VII): HCl, 31.54%. Found HCl, 31.56%, 31.54%, 31.50%. The close agreement in different batches is a fair confirmation of the structure proposed.

The melting point of the material varies from 68-72°C., depending on the rate of heating.

In the preparation of 2,16-dicyano-2,16-dimethyl-3,6,9,12-pentaazaheptadecane pentahydrochloride (IX) the same procedure as for compound (VII) was followed. The hydrochloride salt was formed by passing a current of dry hydrochloric acid through the ethereal solution. In this case the yield was 58% of theory.

Analysis of three different batches for hydrogen chloride by silver nitrate. Calc. for $C_{16}H_{33}N_7.5HCl$: HCl, 36.04%. Found HCl, 36.01%, 36.07%, 36.02%. From this close agreement it is reasonable to assume that the compound was of the proposed structure. The substance melted from 75-82°C., depending on the rate of heating.

3,6-Dinitro-3,7-dicyano-2,7-dimethyl-3,6-diazaoctane (*X*); *3,6,9,12-Tetranitro-2,13-dicyano-2,13-dimethyl-3,6,9,12-tetraazaheptadecane* (*XII*)

0.0516 mole dicyanodimethyldiazaoctane	10 gm.
0.175 mole nitric acid 100%	7.3 cc.
0.52 mole acetic anhydride	48 cc.
0.02 mole acetyl chloride	1.5 cc.

The nitric acid and acetyl chloride were added to the acetic anhydride at 30°C. in a three-necked flask fitted with a "Drierite" drying tube, thermometer, and mercury-sealed mechanical stirrer. The dicyanodimethyldiazaoctane (VI) was then added over a five minute period at 5°C. Upon its addition the dicyanodimethyldiazaoctane dissolved and another fine precipitate formed. This precipitate was probably the nitrate salt and its relative insolubility slows down the reaction. The reaction was kept at 0°C. for 10 min. followed by 24 hr. at 25°C. The mixture was then poured into 1400 cc. of ice and water, the precipitate was filtered off, and washed with water, ethanol, and ether to yield 8.45 gm. of dinitrodicyanodimethyldiazaoctane (60% of theory). The crude product discolored at 130°C., melted with decomposition at 211-212°C.

The crude product can be purified by dissolving 1 gm. of it in 45 cc. of hot nitromethane. Addition of 100 cc. of ether followed by cooling to 0°C. caused the crystalline compound to precipitate. Alternatively 50 cc. of dry acetone and 100 cc. of water may be substituted for the nitromethane–ether. The purified finely divided crystalline compound melted with decomposition at 212-212.5°C. The compound gives a positive test for nitroamine when treated with 1% diphenylamine in concentrated sulphuric acid. It is extremely insoluble in most solvents, except such as nitromethane and acetone in which it can be dissolved with difficulty. This greater solubility in acetone and nitromethane than in other solvents is usual with nitramines.

Following the same process, Compound (XII) was also prepared. The nitrogen analyses are reported in Table II.

3,6,9-Trinitro-3,10-dicyano-2,10-dimethyl-3,6,9-triazaundecane (XI); 3,6,9,12,15-Pentanitro-2,16-dicyano-2,16-dimethyl-3,6,9,12,15-pentaazaheptadecane (XIII)

By using the procedure followed for (X) and (XII), Substances XI and XIII were prepared. Since the starting material was hydrochloride salt, no acetyl chloride was required as catalyst.

The determination of nitrogen for the compounds prepared are reported in Table II.

ACKNOWLEDGMENTS

The authors are indebted to the Defence Research Board of Canada for permission to publish this paper.

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THE POLYMERIZATION OF ISOPRENE AND 2, 3-DIMETHYLBUTADIENE AND COPOLYMERIZATION WITH STYRENE AT −18°C. IN EMULSION[1]

By R. J. Orr and H. Leverne Williams

ABSTRACT

The rate of polymerization increased with purification of the monomers. It was possible that the dienes formed cyclic compounds or dimers in side reactions. The 1,2 addition of the monomer decreased with decreasing polymerization temperature. A study was made of the copolymerization of isoprene and dimethylbutadiene with styrene at −18°C. From analyses of bound diene in the product at various conversions and initial diene to styrene ratios the reactivity ratios for these diene–styrene systems were calculated to be $r_1 = 1.30 \pm 0.02$ and $r_2 = 0.48 \pm 0.01$ for isoprene and styrene and $r_1 = 0.92 \pm 0.02$, $r_2 = 0.42 \pm 0.02$ for dimethylbutadiene and styrene (styrene always being considered monomer 2). Q and e values from the Alfrey–Price equation were calculated as $Q = 1.19$ and $e = -0.112$ for isoprene and $Q = 1.09$ and $e = -0.181$ for dimethylbutadiene relative to $Q = 1.0$ and $e = -0.8$ for styrene. Fom these and the values previously determined for butadiene, reactivity ratios for all combinations of the three dienes were calculated. The chain transfer reaction between dienyl radicals and mixed tertiary mercaptans was studied and it was found that isoprenyl and dimethylbutadienyl radicals were much more reactive than butadienyl. The effect of this was illustrated by number and viscosity average molecular weights. Intrinsic viscosities of homo- and copolymers formed in a mercaptan-free recipe were measured and compared.

INTRODUCTION

General purpose chemical rubbers are produced by copolymerization of butadiene and styrene. It has been shown that a decrease in polymerization temperature yields a superior product (18, 19). Of interest also are the copolymers of styrene with the methyl substituted dienes, isoprene, and dimethylbutadiene. There has been little done in the study of the copolymerization of these dienes even at higher temperatures (7) and no published data are known obtained at lower temperatures. For this reason a study was undertaken of the copolymerization of these dienes with styrene at −18°C.

Recipes have been developed in this (15) and other (4) laboratories which permit copolymerization of butadiene and styrene at −18°C. without undue difficulty and it was felt that these recipes afforded an opportunity for a study of the polymerization behavior of the dienes under conditions in which side reactions and abnormal polymerization reactions are minimized.

EXPERIMENTAL TECHNIQUES

The polymerizations were conducted in 8 oz. peroxide bottles with punctured metal screw caps (5) in which the fiber gasket was replaced by a double rubber gasket consisting of an outer oil resistant Koroseal* sheet and an inner self sealing Butyl** gasket prepared from undercured unpigmented sheet. The techniques have been described in detail (15, 16).

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Contribution from the Research and Development Division, Polymer Corporation Limited, Sarnia, Ont.
Presented before Section IX (Symposium on Copolymerization) of the International Congress of Pure and Applied Chemistry, New York, September, 1951.

*Product of B. F. Goodrich Chemical Company.
**Product of Polymer Corporation Limited.

After the reaction was stopped, the degree of conversion of monomer to polymer was determined (8) and the unreacted monomers were removed from the latex by low pressure steam. The latex was filtered through glass wool to remove precoagulum and coagulated with isopropanol. The polymer was then purified in the conventional manner by reprecipitation from benzene with methanol.

Using the method of Saffer and Johnson (17) the degree of unsaturation was measured. From these results it was possible, in the case of a copolymer, to calculate its composition. The mercaptan in the latex was determined by amperometric titration with silver nitrate (10, 11). The intrinsic viscosities of the polymers formed were measured at 30°C. by dissolving the latex directly in an 80:20 benzene–isopropanol solution. Dilutions were then made with pure benzene so that intrinsic viscosities in pure benzene could be calculated (3, 6, 14).

Monomer purity	Source	Grade	Further treatment
Butadiene	Polymer Corporation Ltd.	Technical	None
Styrene	Polymer Corporation Ltd.	Technical	Steam distilled
Dimethylbutadiene	Polymer Corporation Ltd.		Fractionated
Isoprene	Phillips Petroleum Co.	Research	

Polymerization recipes

	I	II
Monomers	100 parts by wt.	100 parts by wt.
Mixed tertiary mercaptans	0.24	0.24
Water, distilled	157	224
Methanol	46	65.8
Potassium fatty acid soap flakes (Swift and Co.)	5.1	7.3
Daxad 11 (Dewey and Almy Chem. Co.)	0.05	0.07
Potassium sulphate	0.10	0.14
Ferrous sulphate heptahydrate	0.20	0.29
Arsenious oxide	0.2	0.17
Sequestrene AA (Alrose Chem. Co.)*	0.12	0.17
Paramenthane hydroperoxide (Hercules Powder Co.)	0.15	0.22
Ditertiary butyl hydroquinone	0.20	0.29
Benzene	5.0	7.2

**Ethylene diamine tetraacetic acid.*

Initial attempts to synthesize polyisoprene using Recipe I failed. This was ascribed to lack of emulsification, which was immediately evident upon examination of the contents of the bottles. The contents always showed distinctly two phases and never an homogeneous emulsion. This was remedied by increasing the soap and water solution to that amount shown in Recipe II whereupon 40% conversion was obtained in 17 hr. using distilled isoprene. This yield later proved to be decidedly irreproducible, presumably depending on the purity of the sample used. Recipe II was used in all succeeding studies on both isoprene and dimethylbutadiene.

EXPERIMENTAL

Effect of Diene Purity

Two samples of isoprene were obtained, one technical grade analyzing 95% isoprene, and the other Phillips 99 mole % pure research grade. Both samples were fractionated in the usual manner so that the final product had a boiling point range of 0.1 to 0.2°C. On polymerization of these to polyisoprene, 29.4%

conversion was obtained for the sample derived from the technical grade as against 53.6% for the sample derived from the research grade. It was evident that there were impurities inhibiting polymerization which were not removed by fractionation. This experience was borne out with dimethylbutadiene. When samples fractionated from a technical grade were used, 17.5% conversion was obtained in 17 hr. However, when the dimethylbutadiene used was material which had been recovered from low conversion experiments and refractionated, i.e. it had been exposed to the action of free radicals at a low temperature, conversions up to 30% were obtained in the same time. This value was extremely irreproducible indicating that varying degrees of purity were obained in this manner. Proceeding to the effect on the rates of conversion in the styrene–diene copolymer system, it was found that the effect of the inhibiting impurities was much more pronounced than in the homopolymerization systems. This is well indicated by an examination of the data shown in Table I for various dimethylbutadiene–styrene charge ratios using both dimethylbutadiene which had only been fractionated and dimethylbutadiene which had been refractionated after recovery from a low conversion polymerization reaction.

TABLE I

CONVERSION RATE FOR DIMETHYLBUTADIENE–STYRENE COPOLYMERIZATION

Charge ratio, DMB/styrene	Purification procedure	% Conversion/hour, average
75/25	Fractionated	1.1
25/75	Fractionated and recovered	4.7
50/50	Fractionated and recovered	3.5
75/25	Fractionated and recovered	3.0

It seems evident that a very large increase in rates results from use of recovered dimethylbutadiene. In general, the rate of conversion rises as the styrene content of the charge is increased if the purer form of diene is used. However with the more impure grade, the rate decreases as the styrene content is raised. This seems to indicate that the inhibitors normally found in these dienes retard copolymer growth more than homopolymer formation. These results indicate the need for intensive purification of the monomers if any quantitative results are to be deduced from rates of monomer disappearance and if reproducible conversion curves are required for viscosity, residual mercaptan, and other measurements.

Side Reactions

The possibility of side reactions became apparent during the first experiments when a high boiling oil was isolated from reaction mixture in which only low boiling monomers and quite higher molecular weight polymers should have been present. In all experiments these steam volatile compounds were present. From isoprene polymerizations a yellow oil (n_D^{21} 1.493) was obtained together with traces of yellow crystals of a higher melting compound. From dimethylbutadiene polymerizations, larger quantities of the yellow crystals resulted. Since these products were formed in systems where the intrinsic viscosity of the high polymer formed was as high as 6, it was felt unlikely that they could

be low molecular weight linear polymers which would necessarily comprise the lower end of the molecular weight distribution curve. It was thought that they might be cyclic compounds, since it was known that these dienes showed a tendency to cyclize (20).

Effect of Oxygen on Conversion Rates

In the homopolymerizations of butadiene, isoprene, and dimethylbutadiene, the effect of oxygen on the reaction rates was tested (Table II). In the two latter cases oxygen had no effect on the conversion rates and no effect on the intrinsic viscosity of polyisoprene. With butadiene, however, addition of oxygen decreased the rate markedly although little or no change was noted in the intrinsic viscosity.

TABLE II

EFFECT OF OXYGEN ON RATE OF POLYMERIZATION AND VISCOSITY OF POLYMER

Monomer	Cc. air/100 gm. monomers	% Conv. (17 hr.)	$[\eta]$
Butadiene	0	37.5	5.9
	5	18.6	5.1
Isoprene	0	29.4	5.9
	5	33.0	6.0
Dimethylbutadiene	0	17.5	5.5
	5	21.8	—

1,2 and 1,4 Addition

It is known that dienes have alternative methods of chain propagation. Owing to their conjugated structure both 1,2 (or 3,4) and 1,4 addition are possible. Unless the activation energies of the two reactions are identical, the ratio of 1,2 (and 3,4) to 1,4 addition should be a function of temperature. A method (17) has been published whereby this ratio may be determined by measuring the consumption of perbenzoic acid by the polymer as a function of time. Since the acid adds to the 1,4 addition product much more rapidly than to the 1,2 addition product, it is possible to estimate the amount of 1,4 addition. The one difficulty in this method is that in the presence of any 1,2 addition product and of large excess of perbenzoic acid, higher results are obtained for the value of 1,4 addition. This is avoided by obtaining values of the percentage 1,4 addition using different concentrations of perbenzoic acid. From the absolute values of the 1,4 addition and the rate of change of these values with % excess perbenzoic acid, it is in practice quite possible to make a fairly reliable estimate of the true value. This is illustrated by the results obtained using polyisoprene and polydimethylbutadiene synthesized at −18°C. (Table III). It is thus seen that a rather small change in the value occurs with polyisoprene. At 35% excess perbenzoic acid this value is 95% 1,4 addition. From the original work done on the method a value close to the true one would be expected at this perbenzoic concentration. The small change in the value of 1,4 addition supports this view inasmuch as a small amount of 1,2 and 3,4 addition might be expected.

TABLE III
VALUES OF 1,4 ADDITION ON POLYDIENE

Polymer	% Excess perbenzoic acid	% 1,4 Addition
Polyisoprene	115	103
	65	103
	35	95
Polydimethylbutadiene	72	101
	39	101
	32	99.8

For polydimethylbutadiene, there was no significant trend in the value for the % 1,4 addition with all the values close to 100%. This indicates that within the error of this investigation, no 1,2 addition occurs in dimethylbutadiene at this temperature. It is interesting to compare these values with values determined on polymers synthesized at 50°C. This is shown in Table IV. It is thus evident that (i) 1,2 addition decreases more with polymerization temperature with dimethylbutadiene than with isoprene, (ii) 1,2 addition relative to polybutadiene is suppressed at both temperatures by

TABLE IV
CHANGE IN 1,4 ADDITION WITH TEMPERATURE

Polymer	Polymerization temperature, °C.	% 1,4 Addition
Polyisoprene	−18	95
	50	86
Natural rubber		95
Polydimethylbutadiene	−18	100
	50	88

the presence of the methyl groups, presumably because of steric hindrance, and (iii) a product very similar to natural rubber in so far as 1,2 and 1,4 addition is formed at −18°C.

Measurement of Bound Monomer Ratios and Reactivity Ratios of Dienes with Styrene

Measurements of this nature have already been made at −18°C. with butadiene–styrene copolymers (16). The investigation of 1,4 addition by perbenzoic acid addition offered a convenient method for analysis of diene–styrene copolymers by measurement of the total 1,4 unsaturation. In the case of isoprene–styrene copolymers this value was corrected for the fact that only 95% of the isoprene in the copolymer was in the 1,4 configuration. In the dimethylbutadiene–styrene copolymers, however, the 1,4 unsaturation gave the dimethylbutadiene content of the polymer directly. The values obtained at various conversions and charge ratios for the two dienes shown are in Figs. 1 and 2. A statistical analysis of the data shown in these figures gave an average probable error in the results of 0.7% bound diene.

The composition of the copolymer as measured is related to the amount of monomers in the charge at the time of formation of the copolymer by the well-known copolymerization equation. The reactivities of the monomers are ex-

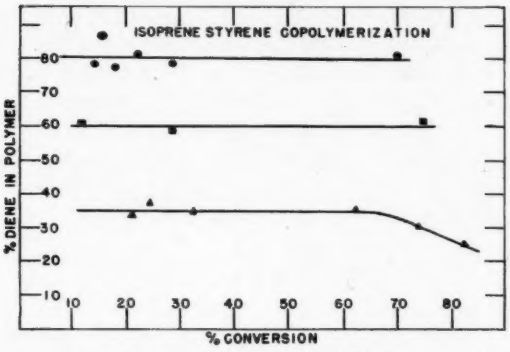

FIG. 1. Bound isoprene for ● 75/25, ■ 50/50, and ▲ 25/75 isoprene/styrene charge ratio.

pressed as a ratio. The reactivity of monomer-1 (r_1) of a pair is the ratio of the rate of reaction of a free radical chain ended in a monomer-1 residue with monomer-1 to the rate with monomer-2. The reactivity ratio of monomer-2 (r_2) is then the ratio of the rate of reaction of a free radical chain ended in monomer-2 with monomer-2 and the rate with monomer-1. The reactivity ratios were calculated by extrapolation of the bound monomer curves to 0% conversion and substitution of the values obtained in the copolymerization equation. This method was made necessary because it was only here that the actual ratio of monomers was known in the absence of quantitative data on the possible side reactions. If the diene is considered as monomer 1, then the reactivity ratios obtained were $r_1 = 1.30 \pm 0.02$ and $r_2 = 0.48 \pm 0.01$ for isoprene–styrene, and $r_1 = 0.92 \pm 0.02$ and $r_2 = 0.42 \pm 0.02$, for dimethylbutadiene–styrene. The limits of error were determined by the degree to which the results from each charge ratio checked with each other.

Recalling $r_1 = 1.37$ and $r_2 = 0.38$ for the butadiene–styrene system at this

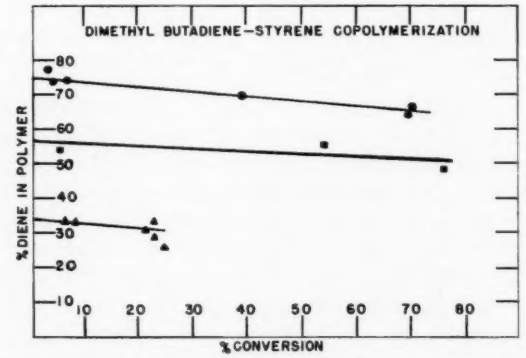

FIG. 2. Bound dimethylbutadiene for ● 75/25, ■ 50/50, and ▲ 25/75 DMB/styrene charge ratio.

temperature (16) it is evident that as the number of methyl groups on the diene increase, r_1 shows a continual decrease. This means that with increasing substitution, the dienyl free radicals show an increasing preference to attack styrene over attacking a diene molecule; r_2 seems to rise to a maximum for isoprene.

An attempt to describe all copolymerization characteristics of a monomer in terms of two constants Q and e has been recently made by Alfrey and Price (1) which are defined in terms of the equations

$$r_1 = \frac{Q_1}{Q_2} e^{-e_1(e_1-e_2)} \text{ and } r_2 = \frac{Q_2}{Q_1} e^{-e_2(e_2-e_1)}.$$

Q is a measure of the reactivity of the monomer and e a measure of its polar character. For purposes of this treatment Q and e for styrene were arbitrarily chosen as 1.0 and -0.8 respectively.

Solving the above equations we obtain a $Q = 1.09$ and $e = -0.181$ for dimethylbutadiene and $Q = 1.19$, $e = -0.112$ for isoprene. Recalling that butadiene (16) shows a $Q = 1.38$ and $e = +0.008$ it is evident that addition of methyl groups causes a continuous decrease in the values of Q and e.

Possibly the most interesting use to which these constants could be put is a calculation of r_1 and r_2 for monomer pairs which had not been measured directly. This was done for the various diene combinations and the results are shown in Table V.

TABLE V
CALCULATED REACTIVITY RATIOS

Monomers	r_1	r_2
Butadiene and isoprene	0.94	1.06
Butadiene and dimethylbutadiene	1.26	0.78
Isoprene and dimethylbutadiene	1.18	0.84

Since the direct determination of these constants is subject to severe analytical difficulties, even an approximation, such as these values are, is of possibly greater accuracy than those which would be measured directly.

Bound Diene of Increment Polymer and Residual Unreacted Diene

The bound diene of the increment polymer is the average composition of the polymer formed over an increment of conversion. Since the composition of the unreacted monomers is continually subject to change, and side reactions are probably taking place, the composition of polymer formed changes as reaction proceeds. This chemical heterogeneity has a rather large effect on the properties of the polymer. In Table VI is shown bound diene of the increment polymer for dimethybutadiene–styrene copolymers calculated from the smoothed curves of Fig. 2.

With isoprene the bound diene is constant over the conversion range at 80.5, 60.0, and 36.0 for 75/25, 50/50, and 25/75 diene/styrene charge ratios.

TABLE VI

BOUND DIENES OF INCREMENT POLYMER FOR DIENE–STYRENE COPOLYMERS

Diene	% Conv. range	% Diene in copolymer formed for initial diene/styrene charge ratio		
		75/25	50/50	25/75
Dimethylbutadiene	0–10	73	56	33
	10–20	71	54	31
	20–30	69	52	
	30–40	67	52	
	40–50	65	48	
	50–60	63	50	
	60–70	61	47	

With dimethylbutadiene the diene content of the increment polymer decreases more rapidly than with isoprene.

The per cent unreacted diene in the residual monomers, assuming no side reaction, was also calculated (Table VII).

TABLE VII

RESIDUAL UNREACTED DIENE

Diene	% Conversion	% Diene in residual monomer for initial diene/styrene charge ratio		
		75/25	50/50	25/75
Dimethylbutadiene	10	75	50	24
	20	76	49	23
	30	77	48	
	40	79	48	
	50	81	47	
	60	84	48	
Isoprene	10	74	49	25
	20	74	48	22
	30	73	46	20
	40	72	43	18
	50	70	40	14
	60	67	30	9
	70	63		

The values of the bound diene of the increment polymer should be related to the values for residual diene in the unreacted monomers and the reactivity ratios r_1 and r_2 by the equation $\frac{dD}{dS} = \frac{D}{S}\left(\frac{r_1 D/S + 1}{D/S + r_2}\right)$ where S is the concentration of styrene and D the concentration of diene. When the calculated unreacted diene in the residual monomer is plotted against the calculated increment polymer composition, for a given set of reactivity ratios, the theoretical lines shown in Fig. 3 are obtained. When the observed values are plotted in this manner, it will be noted that only for 0% conversion do the values agree. At all finite values of conversion, there is a drift from the values predicted by the reactivity ratios. The cause of this is unknown but it should be noted that the drift is in the direction of a less random polymer, i.e. at higher conversions

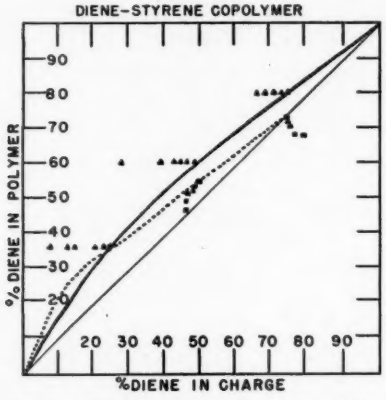

FIG. 3. Increment bound diene against residual diene in charge.
——— Calculated curve for isoprene–styrene $r_1 = 1.30$; $r_2 = 0.48$.
– – – Calculated curve for DMB–styrene $r_1 = 0.92$; $r_2 = 0.42$.
▲ Observed values for isoprene–styrene copolymerization.
■ Observed values for DMB–styrene copolymerization.

there is a greater tendency to an alternating copolymer than the values of the reactivity ratios can account for except for r_1 of the dimethylbutadiene system which tends to increase. This type of behavior was also noticed in the butadiene–styrene system at this temperature (16) but in that case the values of r_1 and r_2 both tended to increase.

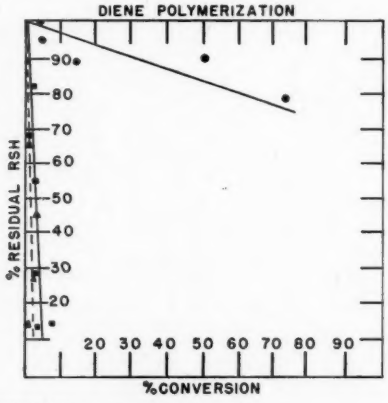

FIG. 4. MTM disappearance curves for:
● butadiene, ■ isoprene, and ▲ dimethylbutadiene.

Modifier Disappearance Curves

The reactivity of the free radical toward mercaptans is of considerable importance in the industrial applications of polymerization since this is one of the most widely used methods of regulating the molecular weight of the product. The rate of disappearance of mercaptan gives a measure of the relative impor-

tance of this chain transfer reaction. Three dienes, isoprene, butadiene, and dimethylbutadiene were investigated with MTM,* at a concentration of 0.39 parts MTM/100 parts monomers. The data for the three dienes are shown in Fig. 4. It is evident that the mercaptan disappears much more rapidly in the isoprene and dimethylbutadiene systems than it does in the butadiene systems. Assuming that the logarithm of the % residual mercaptan is linear with respect to % conversion, the slopes of the lines were calculated. These are the regulating indices given in Table VIII.

TABLE VIII
REGULATING INDEX FOR MTM

Monomer	Regulating index
Butadiene	0.4
Isoprene	40
Dimethlybutadiene	52

Two factors influence this regulating index, (i) the absolute rate of the chain transfer reaction, (ii) the rate of diffusion of the mercaptans to the growing polymer free radicals. In the event of a rapid diffusion the regulating index then becomes a measure of the reactivity of the free radical toward the mercaptan. In this particular recipe, diffusion must be relatively rapid since the regulating index is high. This indicates that isoprenyl and dimethylbutadiene radicals show a reactivity of at least 90 to 100 times greater toward MTM than do butadienyl radicals. This result is supported by work on dimethylbutadiene (12) which indicates that less modifier is required to synthesize a polymer of a given Mooney viscosity than is the case for butadiene systems and by observations that isoprene in the presence of chain transfer agents yields oils (2). No work has been done on diene–styrene copolymerization systems but there

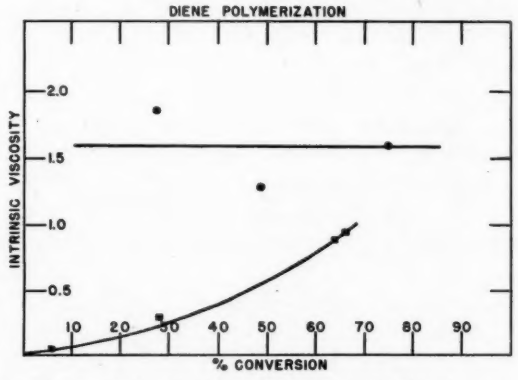

FIG. 5. Intrinsic viscosity with 0.39 parts MTM of:
● polybutadiene and ■ polyisoprene.

** A mixed tertiary mercaptan consisting of 60%C_{12}, 20%C_{14}, 20%C_{16} average molecular weight, 220. Phillips Petroleum Company.*

is no reason to believe that this increase in modifier consumption will not also be characteristic of the copolymerizing systems.

It is interesting to note the effect of this increased mercaptan consumption on the intrinsic viscosity of the polymer produced. This is shown in Fig. 5 for butadiene and isoprene. It will be noted that the intrinsic viscosity for polybutadiene is relatively constant (see also Reference 16) while that for polyisoprene begins at a very low value and slowly rises. This increase is due to the fact that at 10 to 15% conversion, all the mercaptan has been consumed and the polymer is then being formed in a mercaptan free medium. Although the data are very scattered, it is of interest to calculate the intrinsic viscosity of the increment polymer being formed and show how it increases when the mercaptan has been consumed. This is shown below in Table IX using the smoothed curves of Fig. 5 for isoprene.

TABLE IX

INCREMENT INTRINSIC VISCOSITIES FOR POLYISOPRENE

% Conversion range	Intrinsic viscosity
0–10	0.05
10–20	0.15
20–30	0.40
30–40	0.80
40–50	1.25
50–60	1.85
60–70	3.20

It may be seen (Fig. 5) that the increment intrinsic viscosity in polybutadiene is constant at 1.60. This is also characteristic of butadiene–styrene copolymers at this temperature (16). However the increment intrinsic viscosity of the polyisoprene slowly rises, indicative of the fact that the mercaptan is disappearing exceedingly rapidly. There is no apparent reason why there is not a sharp increase in this increment intrinsic viscosity to a value which would be characteristic of a mercaptan free system when the mercaptan is consumed.

Number Average Molecular Weights

Assuming that the only chain terminating step is that due to mercaptan it is possible to compare number average molecular weights for the two systems. The number average molecular weights for polybutadiene calculated from the smoothed curve of Fig. 5 is 1.1×10^5. The data for polyisoprene are in Table X.

TABLE X

CALCULATED MAXIMUM NUMBER AVERAGE MOLECULAR WEIGHTS FOR POLYISOPRENE

% Conversion	$\bar{M}_n$
2	2.8×10^3
4	3.2×10^3
10	5.6×10^3

For isoprene, however, $\bar{M}_n$ increases after the total consumption of the mercaptan, the increment $\bar{M}_n$ to a value representing other types of termination.

Intrinsic Viscosities with a Mercaptan Free Recipe

One characteristic of −18°C. reactions is that it is possible to prepare soluble diene polymers and copolymers in mercaptan free recipes. This is not possible at higher temperatures where the greater proportion of cross linking and branching gives insoluble polymers. The intrinsic viscosity was measured at different charge ratios and conversions. The data for isoprene–styrene copolymerization reactions are shown on Fig. 6. It will be noticed that for the higher diene con-

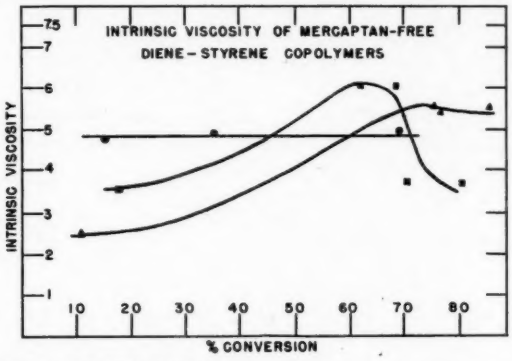

FIG. 6. Intrinsic viscosities for:
●, ■, ▲ 75/25, 50/50, and 25/75 isoprene–styrene.

tents, the intrinsic viscosity seems to be independent of conversion but a peak at about 50% conversion may have been missed. At higher styrene contents (50/50 and 25/75 diene/styrene charge ratio) this is no longer the case. The curves seem to pass through maxima. Some data for dimethylbutadiene–styrene copolymerization reactions are in Table XI.

TABLE XI

INTRINSIC VISCOSITIES OF UNMODIFIED DIMETHYLBUTADIENE–STYRENE COPOLYMERS

Charge ratio	% Conversion	[η]
75/25	23.5	3.3
	31.7	2.6
50/50	14.4	2.0
	31.7	3.5
25/75	29.4	3.2
	31.2	3.9

It may be seen that the intrinsic viscosities of the three polydienes prepared in mercaptan free recipes are very nearly equal (Table II). The initial intrinsic viscosity of the polymer formed becomes lower as the styrene content of the polymer increases. This is shown in Table XII for isoprene–styrene copolymers.

The intrinsic viscosities for dimethylbutadiene–styrene copolymers were always lower than the corresponding isoprene–styrene copolymers. (Compare Table XI with Fig. 6.) The change in [η] between 75/25 and 50/50 charge ratio also seemed to be less than the corresponding change in the isoprene–styrene system.

TABLE XII

INTRINSIC VISCOSITIES AT 0% CONVERSION FOR ISOPRENE–STYRENE COPOLYMERS

Charge ratio isoprene/styrene	Intrinsic viscosity at 0% conv.
100/0	6.0
75/25	4.9
50/50	3.4
25/75	2.4

Viscosity Average Molecular Weights of Polyisoprene

If we assume that K and a for the polydienes are not appreciably different, and since K and a for polybutadiene synthesized at this temperature is suggested to be $K = 10.6 \times 10^{4}$ and $a = 0.63$, it is possible to calculate viscosity average molecular weights (9) for the modified polybutadienes and polyisoprenes. These are in Table XIII for polyisoprene.

TABLE XIII

VISCOSITY AVERAGE MOLECULAR WEIGHTS OF MODIFIED POLYISOPRENE

% Conversion	Polyisoprene
10	4.6×10^{3}
20	1.3×10^{3}
30	4.0×10^{3}
40	9.7×10^{3}
50	1.8×10^{4}
60	5.0×10^{4}
70	6.3×10^{4}

The viscosity average molecular weight of polybutadiene is constant at 1.1×10^{5} assuming a horizontal line in Fig. 5. However, the viscosity average molecular weight of polyisoprene increases quite rapidly as would be expected from the modifier disappearance data, Fig. 4, and as calculated from the smoothed curve of Fig. 5.

DISCUSSION

The change in Q and e values as the number of methyl groups increase is interesting; e is usually defined as $C/\sqrt{DkTr}$ (1) where

C is charge on double bond,
r is radius of activated complex,
D is dielectric constant,
k is Boltzmann's constant, and
T is the absolute temperature.

If r is assumed to be constant for the different dienes, then C must become increasingly more negative with the addition of methyl groups since a change in the dielectric constant D has been shown not to affect reactivity ratios. Recalling that e was $+0.008$, -0.112, and -0.181 for butadiene, isoprene, and dimethylbutadiene respectively, it may be seen that the Δe caused by addition of a methyl group decreases from -0.120 for the first methyl group to -0.069 for the second.

A survey of the data in a recent comprehensive review by Mayo and Walling (7) was made. There appeared to be two series in which comparisons of monomers and their methyl analogue could be made. The first is in Table XIV in which the reactivity ratios for methyl acrylate and methyl methacrylate in combination with a number of reference monomers is shown. It will be observed that in all cases r_1 increases and r_2 decreases with methyl substitution; quite contrary to our observations.

TABLE XIV

COMPARISON OF REACTIVITY RATIOS

M_2 \ M_1	Methyl acrylate			Methyl methacrylate		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
Allyl acetate	5	0		23	0	
Butadiene	0.05	0.76	0.038	0.25	0.75	0.19
2-Chloroallyl acetate	0.7	0		1.0	0	
2-Chlorobutadine	0.081	11.1	0.90	0.083	6.12	0.51
2, 5-Dichlorostyrene	0.15	3.4	0.51	0.44	2.25	0.99
Maleic anhyd.	2.8	0.02	0.056	6.7	0.02	0.13
Trichloroethylene	3.5	0		81	0	
Vinyl chlor.	9.0	0.083	0.74	13	0	
Styrene	0.206	0.775	0.18	0.49	0.56	0.27

The second series shows the reactivity ratios for a number of monomers and their methyl derivatives towards styrene and methyl methacrylate as reference monomers, Table XV. Again r_1 and r_2 increase and decrease respectively except for butadiene, styrene, and vinyl acetate in which the opposite tendency is shown. The only distinguishing feature of these three monomers is the negative "e" value. Whether this is a general rule and whether it has a satisfactory explanation should be left for further data.

TABLE XV

COMPARISON OF REACTIVITY RATIOS

				Methyl analogue		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
Styrene = M_2						
Butadiene	1.83	0.65	1.2	1.68	0.80	1.3
Acrylic acid	0.25	0.15	0.038	0.7	0.15	0.11
Acrylonitrile	0.03	0.42	0.012	0.18	0.30	0.27
Allyl acetate	0	90		0	71	
Allyl chloride	0.016	31.5	0.50	0	22	
Methyl acrylate	0.206	0.775	0.16	0.49	0.56	0.27
Methyl methacrylate = M_2						
Vinyl acetate	0.015	20	0.30	0.017	30	0.51
Acrylonitrile	0.18	1.35	0.24	0.65	0.67	0.44
Allyl acetate	0	23		0	10	
Allyl chloride	0	41		0	7.5	
Styrene	0.56	0.49	0.27	0.14	0.50	0.07

Considerably less data are available on the changes of Q and e values with methyl substitution so that the data in Table XVI might be considered as indicative of possible trends. In this field many more data are required.

TABLE XVI

COMPARISON OF Q AND e VALUES

			Methyl analogue	
	Q	e	Q	e
Butadiene	1.38	0.008	1.09	−0.181
Styrene	1.0	−0.8	0.58	−1.0
Methyl methacrylate	0.42	0.6	0.74	0.4

A method has recently been published (13) whereby an estimate of the heterogeneity of the molecular weight of a polymer may be made if viscosity average and number average molecular weights are known. For GR-S the relationship was calculated as

$$\beta = 2.35\sqrt{\log R} \text{ and } M_0 = \bar{M}_n R^{-0.60} \text{ where } R = \frac{\bar{M}_v}{\bar{M}_n}.$$

β is a measure of the heterogeneity of the polymer and M_0 is that molecular weight at which the peak occurs in the distribution curve. It may be seen from the data that for polybutadiene $\beta = 0$ and $M_0 = \bar{M}_v = \bar{M}_n = 1.1 \times 10^5$. This indicates the highly improbable condition of a completely homogeneous polymer. Polyisoprene showed $\bar{M}_v < \bar{M}_n$. This obviously cannot be the case and indicates that the experimental errors involved are very large or the considerations do not apply under the experimental conditions used.

From the theoretical side it is evident that some means of expressing reactivities which takes into account the "activity" of the double bond and the effect of temperature is required. Perhaps then the effect of substitution adjacent to the double bond can be predicted with more certainty as a function of the activity of the original structure. In the more practical field it has been shown that isoprene and dimethylbutadiene polymerize and copolymerize much like butadiene but are more sensitive to monomer impurities, less sensitive to oxygen, and more difficult to modify to form a product of more uniform molecular weight. On the other hand there is more tendency towards a linear structure so that high conversion linear polymers should be possible as well as soluble polymers of very high molecular weight.

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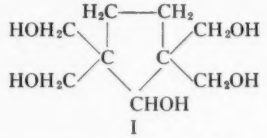
2, 2, 5, 5-TETRAMETHYLOLCYCLOPENTANOL PENTANITRATE[1]

By D. C. Downing[2]

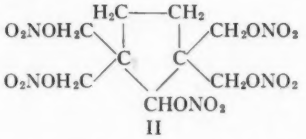
ABSTRACT

Tetramethylolcyclopentanone was hydrogenated (70% purified yield) and nitrated (74% purified yield) to give 2,2,5,5–tetramethylolcyclopentanol pentanitrate, m.p. 91°, a powerful explosive only slightly weaker than RDX. A number of its properties were determined.

2,2,5,5–Tetramethylolcyclopentanol (I) was prepared by hydrogenation of the corresponding cyclopentanone, the condensation product of cyclopentanone with 4 moles of formaldehyde (2, 3). The pentanitrate (II) was prepared for evaluation as an explosive.



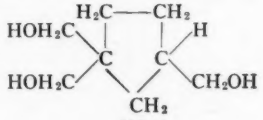
I



II

Hydrogenation was carried out in absolute ethanol in a rocking bomb using copper chromite catalyst. Pure I melts at 97.5°, but crystallization was induced with difficulty unless seeding was used.[3] From a series of hydrogenations the best yield of crystalline I, m.p. 95–96.5°, was 70% of theory. It was found that a hydrogen absorption 120–140% of theoretical was necessary for a good yield. The purer the starting material (tetramethylolcyclopentanone) the less was the margin of actual over theoretical hydrogen absorption. If the melting point of the starting ketone was lower than 142° (pure, 144°), little or no product was obtained. The 70% yield was obtained with 3.4 ml. ethanol per gram of ketone. Using 2 ml. per gram, a 65% yield was obtained; with 1.2 ml. per gram the yield was 29% and unchanged ketone was present, even though hydrogen uptake was over theoretical. The optimum reaction temperature appeared to be 145-160°. Hydrogen pressure was varied from 1900 to 3000 p.s.i. (at 25°) without any observable effect on the reaction.

Small amounts of a second hydrogenation product were purified to a white solid, m.p. 108.2° to 108.5°, which analyzed fairly satisfactorily for trimethylolcyclopentane (III). The additional hydrogen required for this or similar



III

[1] *Manuscript received October 11, 1951.*
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[2] *Present address: Shawinigan Chemicals Limited, Shawinigan Falls, Que.*

[3] *Actually the first crystalline I was a sample, m.p. 96°, prepared by Dr. L. W. Cooke at McGill University in a preliminary run before systematic investigation was started.*

products is probably the reason for the lower yields obtained, when reaction was stopped at theoretical hydrogen uptake.

Nitration of I could be carried out either with a large excess of concentrated (over 95%) nitric acid alone, or with mixed acid. With nitric acid a larger excess was required and the product remained in solution. Precipitation of it later in clean form was difficult—it tended to come down as a gummy mass. When mixed acid was used the pentanitrate precipitated and could be filtered off at the end. Almost all the II prepared was nitrated in a mixed acid containing 400% of theory of 99% nitric acid, plus enough concentrated sulphuric acid to give a final sulphuric acid to water ratio corresponding to $H_2SO_4.H_2O$. This is an acid of approximate composition HNO_3 61%, H_2SO_4 36.6%, and H_2O 2.4%, using almost exactly 10 parts by weight acid per part of I. When nitration was carried out close to 5°C., the product filtered off without dilution was 79–80% of theory. Dilution with water gave a higher yield, up to 91–92%, but the material was gummy and difficult to wash.

In the laboratory a convenient purification procedure for the pentanitrate was to filter it from the mixed acid on a sintered glass filter, then drown the damp product in stirred cold water. The II was then filtered off, washed, and melted under fresh water. Steam was passed through for a few minutes, and the explosive drawn off into acetone. When the acetone solution was added to water, the product was precipitated in clean granular form in about 75% over-all yield, m.p. 90.5° (pure, 91°). The vacuum stability of this material was not raised by crystallization from ethanol.

Tests of the explosive properties of II place its explosive power higher than tetryl and below RDX. Sensitivity to direct impact was about the same as RDX, while that to sliding friction appeared to be somewhat less. The Abel test and vacuum stability at 95–100° showed that some decomposition was taking place at those temperatures. In view of the complicated preparation of II, it seems unlikely that it would be found to have any advantage over explosives in current use.

EXPERIMENTAL[4]

2,2,5,5–Tetramethylolcyclopentanol (I)

A laboratory rocking hydrogenation bomb was used. A liner (steel) was found desirable, to prevent splashing of starting material which otherwise blocked the line to the pressure gauge. In the bomb were placed 102 gm. of tetramethylolcyclopentanone (crystd. from ethanol, m.p. 143°), 350 ml. absolute ethanol, and 8 gm. copper chromite catalyst (1). Electrolytic hydrogen was added to 1910 p.s.i. at 25°, and reaction carried out for 40 min. at 145–150°. At the end of that time hydrogen uptake was 130% of theory; the rocker was stopped and the bomb allowed to cool. Catalyst was filtered off on a Büchner with a precoat of Johns-Manville Super–Cel, and the filtrate evaporated to syrup at water pump vacuum below 60°. The pale green syrup was dissolved in 500 ml. hot dioxane, filtered hot, and cooled to 0° with seeding

[4] *Melting points corrected for thermometer error and stem exposure.*

and mechanical stirring. After several hours' stirring, 72.4 gm. (70% of theory) of I was filtered off, m.p. 95° to 96.5°.

A sample of similar material was crystallized twice from methyl ethyl ketone to give white crystalline solid, m.p. 97.5°.

Calculated for I, $C_9H_{18}O_5$: C, 52.41; H, 8.80.

Found: C, 52.5, 52.6, 52.6; H, 8.62, 8.96, 8.71.

Hydrogenation By-product (III?)

After crystallization of a crude hydrogenation product by cold stirring with methyl ethyl ketone, the filtrate was evaporated partially in vacuum below 50°, to give a second crop melting sloppily at 100–104°. This was crystallized three times from methyl ethyl ketone, once from dioxane, and twice more from methyl ethyl ketone, to give a white solid melting sharply at 108.2 to 108.5°.

Calculated for III, $C_8H_{16}O_3$: C, 59.97; H, 10.07.

Found: C, 60.84, 60.42, 59.68; H, 10.52, 10.67, 10.52.

2,2,5,5-Tetramethylolcyclopentanol Pentanitrate (II)

A mixed acid was made up from 1390 ml. of 99% nitric and 710 ml. of 95.5% sulphuric acids. To this, stirred and held below 7°, was added gradually 338.8 gm. of I (m.p. over 94°) over 145 min. (In this run, 560 ml. water was added below 11° at the end, a procedure not recommended: it promotes decomposition without raising the yield. Filtration without dilution is better.) The crude nitration product was filtered and sucked on sintered glass, drowned in 1600 ml. stirred cold water, refiltered on paper, and washed until the washings were not acid to Congo red paper. The crude product was 563 gm. (79% of theory), m.p. 90.5°, pale pink. It was purified by melting under two parts water, blowing steam gently through the explosive layer for 10 min., then drawing off the explosive layer into 1500 ml. acetone. The filtered acetone solution was added over 50 min. to 4500 ml. water containing just enough ammonia to keep it barely basic to phenol red. The water was stirred violently and held below 15°. The purified II filtered off weighed 534 gm. (74% of theory), m.p. 90.5°, in granular form with an almost imperceptible pink tinge.

A sample of crude II, m.p. 87–89°, was crystallized rapidly from boiling benzene (3.3 ml. per gram) and then from 95% ethanol (22 ml. per gram) to give a white crystalline solid, m.p. 91°.

Calculated for II, $C_9H_{13}N_5O_{15}$: C, 25.07; H 3.04; N, 16.24.

Found: C, 25.5, 25.3, 25.4; H, 3.04, 3.10, 3.03; N (Dumas), 16.5, 16.2.

Explosive Tests on II

In the ballistic mortar of the Explosives Laboratory in Ottawa, loose II had a power 1.51 times TNT (tetryl about 1.3, RDX 1.61). In an impact sensitivity apparatus the 50% firing height was 95 cm. (RDX, 82 cm.). A 6 lb. sliding weight on a 30° incline, whose 50% firing position for RDX was 40 cm., did not fire II when released at a height of 150 cm. (NENO, dinitroxyethyldinitrooxamide, is not fired at 150 cm. either). When ground vigorously in

an unglazed porcelain mortar a slight crackling was observed; this is noted regularly with PETN, but not with RDX or NENO.

The Abel heat test at 100° of II was 15–35 min. The vacuum stability (5 gm. sample) at 80° was such that after the first 60 min. no appreciable gas (below 0.5 ml.) was evolved in 48 hr. At 95° acetone precipitated samples gave 11–13 ml. in 24 hr.; ethanol crystallized samples gave slightly more, over 14 ml. At 100° the gas was 12–15 ml. in 12 hr., with no difference observed between precipitated and crystallized samples.

ACKNOWLEDGMENTS

Assistance in some of the hydrogenations was given by K. K. Carroll. Microanalyses were carried out by Mrs. P. M. Marrian and Mrs. C. Barker.

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THE CONDUCTANCES OF STRONG SOLUTIONS OF STRONG ELECTROLYTES AT 95°[1]

By A. N. Campbell and E. M. Kartzmark[2]

ABSTRACT

Measurements of conductance and fluidity of silver nitrate and of ammonium nitrate solutions, over a range of concentration varying from 0.05 *N* to 14 *N* (silver nitrate) and from 0.08 *N* to 15 *N* (ammonium nitrate) have been made. In both cases, a maximum is observed in the specific conductances but in neither case does a minimum occur in the plot of equivalent conductance against concentration. While the equivalent conductance in very dilute solutions is proportional to $\sqrt{C}$, in very concentrated solutions it appears to be directly proportional to *C*. Temperature coefficients of conductance and of fluidity are evaluated and their theoretical importance discussed. Partial molar volumes of water in these solutions are evaluated.

This paper is a continuation of previous work by the authors (1) on the conductances of strong solutions of silver nitrate and of ammonium nitrate at 25°C. The increased solubility at 95° permits the measurements to be pushed to higher concentrations (14 molar with silver nitrate,—82% by weight, and 15 molar with ammonium nitrate—85% by weight).

EXPERIMENTAL PROCEDURE

Full experimental details are given in the original papers (1). Two experimental difficulties arose as a result of the high temperature. They were:—(1) maintaining a thermostat at 95° and (2) removing dissolved air from the solutions. The thermostat was jacketed with a 2 in. layer of asbestos powder and felt; the perforated lid was covered with a 1 in. layer of felt. The oil was stirred with three Archimedean stirrers, resulting in temperature control of ± 0.05°. The temperature of 95.00°C. was determined by means of a Beckmann thermometer calibrated three times against a certificated mercury-in-glass thermometer, both thermometers being completely immersed in a stirred and electrically heated oil bath.

To remove dissolved air the solvent was boiled for half an hour, salt added, and the solution brought to boil under reduced pressure. This treatment resulted in a loss of an unknown amount of water and hence the solutions had to be analyzed. The obvious methods of analysis, viz. deposition of silver from cyanide solution and the Kjeldahl method for ammonia were not entirely satisfactory, so the solutions were analyzed conductometrically by determining their specific conductances at 25°. From the previously determined specific conductances of solutions of known concentration (1) the weight percentage was obtained; density determinations at 95° then gave the molarities at 95°. Solutions with concentrations greater than the solubility at 25° were diluted by weight to fall within the 25° range.

The cell constants ranged from 800 to 1200. They were determined in the usual manner, by use of potassium chloride, at 25°. No accurate data exist for the specific conductances of potassium chloride solutions at 95°. The effect

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Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.
[2] *Holder of a Studentship under the National Research Council of Canada, 1950-51.*

of a 70° rise in temperature on the linear dimensions of a cell constructed of pyrex glass and platinum must be very slight. These cells were not perfectly designed for elimination of the Parker effect (2) but this is neglible with highly conducting solutions. Indeed, the precautions necessary for these strong solutions are quite different from those of dilute solutions, e.g. the solvent correction is unnecessary.

Because of the possibility of acid hydrolysis, in ammonium nitrate solutions, the pH of a 13.38 *N* solution of ammonium nitrate was determined, after it had been boiled under reduced pressure in the usual way to remove dissolved air. The figure obtained was 4.5. This hydrogen ion concentration is much too low to have any effect on our conductance measurements.

EXPERIMENTAL RESULTS AND DISCUSSION

Table I contains the results of the measurements of conductance and of viscosity. A maximum of specific conductance occurs at a concentration between 10 and 10.5 molar, at 95°, in the case of silver nitrate, and at 8.0 molar for ammonium nitrate. Such a maximum is lacking in the 25° measurements for silver nitrate, presumably because the solubility does not permit of measurements beyond 9.709 molar, whereas, for ammonium nitrate, the maximum occurs at the same concentration, viz. 8.0 molar (1). It is interest-

TABLE I

CONDUCTANCES, DENSITIES, AND VISCOSITIES OF SOLUTIONS OF SILVER NITRATE AND OF AMMONIUM NITRATE AT 95° C.

Wt. %	Molarity	Specific conductance, mhos	Equivalent conductance	Density, gm./ml.	Relative viscosity ($H_2O = 1$)
A. Silver nitrate					
0.9363	0.0534	0.0159	298.3	0.9696	0.9928
18.572	1.220	0.2107	172.7	1.116	1.122
29.70	2.189	0.3236	147.8	1.252	1.263
36.954	2.967	0.3881	130.8	1.364	1.425
50.735	4.829	0.4979	103.1	1.617	1.797
60.46	6.591	0.5595	84.88	1.852	2.280
69.54	8.830	0.6015	68.12	2.157	3.107
73.38	9.906	0.6071	61.28	2.293	3.590
79.45	11.876	0.5982	50.35	2.540	4.262
82.33	14.02	0.5620	40.08	2.816	....
B. Ammonium nitrate					
0.728	0.0878	0.0269	306.2	0.9656	....
1.605	0.1940	0.0534	275.3	0.9677	1.016
8.041	0.9963	0.2340	234.8	0.9918	1.054
12.119	1.525	0.3257	213.6	1.0071	1.076
19.895	2.576	0.4781	185.6	1.0365	1.142
26.96	3.600	0.6008	166.9	1.069	1.217
31.116	4.221	0.6529	154.7	1.086	1.296
38.13	5.325	0.7219	135.6	1.118	....
45.89	6.632	0.7696	116.0	1.157	1.555
53.12	7.95	0.7776	97.81	1.198	1.777
57.50	8.74	0.7695	88.04	1.217	1.913
64.65	10.12	0.7318	72.44	1.253	2.381
69.54	11.13	0.6898	61.99	1.281	2.705
79.74	13.31	0.5599	42.07	1.336	3.89
85.58	14.81	0.4252	28.71	1.385	4.29

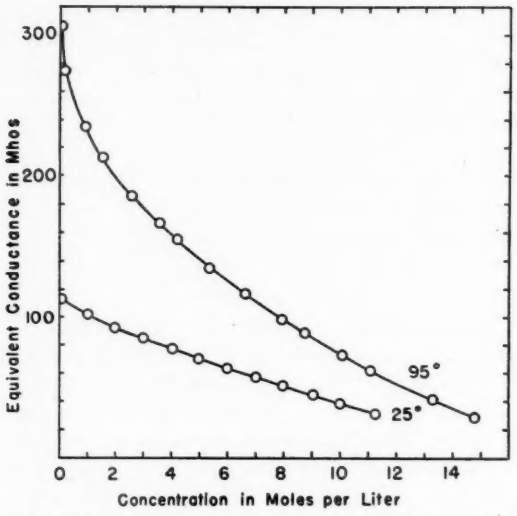

FIG. 1. Conductance vs. concentration of ammonium nitrate solutions.

ing that the concentration of the maximum should be the same, especially as the plot of specific conductance against concentration shows higher curvature at the higher temperature.

When equivalent conductance is plotted against molarity, smoothly descending curves, approaching linearity at high concentration, are obtained in each case, analogous to those at 25° (Figs. 1 and 2).

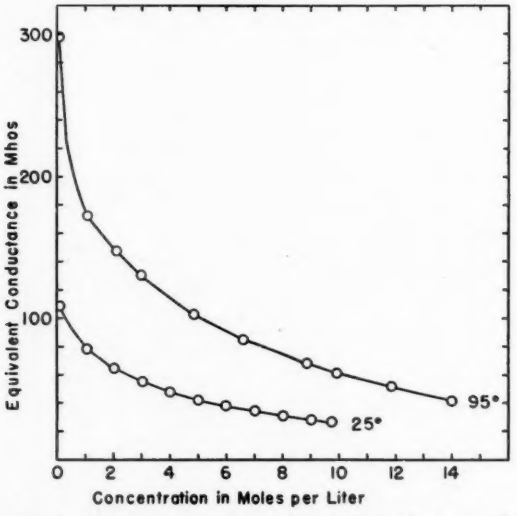

FIG. 2. Conductance vs. concentration of silver nitrate solutions.

The approach to linearity is so very marked that we have calculated the equivalent conductance, assuming a linear relation, from the experimental conductances at the two highest concentrations, for silver nitrate and ammonium nitrate respectively, both at 95°. The results are given below:

Molarity	Λ calc.	Λ obs.
Ammonium nitrate		
11.13	62.0	61.99
10.12	71.5	72.44
8.74	83.5	88.04
Silver nitrate		
9.906	61.0	61.28
8.83	65.5	68.12

It will be interesting to find whether this linear relation persists at still higher concentrations. According to Walden (3), a minimum may occur in agreement with the relation:

$$C_{\min} = k\, D^3$$

where k is a characteristic constant and D is the dielectric constant of the solvent. Because of the high value of D for water, $C_{\min}$ will lie at very high concentrations (greater than 14 molar for silver nitrate and greater than 15 molar for ammonium nitrate).

Table II contains the equivalent conductances, temperature coefficients of conductance, fluidities, and temperature coefficients of fluidity. The temperature coefficients are obtained on the quite erroneous assumption that both conductance and fluidity are straight line functions of the temperature, whereas in fact conductance is expressed by the virial equation, $\Lambda_t^\circ = \Lambda_{25}^\circ(1+a\ (t-25)+b\ (t-25)^2+\ldots)$ and fluidity by an exponential equation, $f_t^\circ = A^{-1}\ e^{-\frac{\Delta E_{\text{vis}}}{RT}}$. For purposes of rough comparison, however, the treatment is sufficient. The coefficients are expressed graphically as functions of molarity in Fig. 3. The graphs run roughly parallel; temperature coefficient of fluidity is higher than that of conductance. Table II also contains the ratio, γ/β, of coefficient of fluidity to coefficient of conductance. This ratio is interesting from at least two points of view. In the first place it is never unity, even in the most dilute solutions. For very dilute solutions, the temperature coefficient of conductance is supposed to be about the same as the coefficient of fluidity of water, viz. about 0.02. The figures show that in concentrated solutions the fluidity increases with temperature more rapidly than does the conductance. Hence a factor, opposing the increase of conductance due to increase of fluidity alone, must exist in these solutions. It is remarkable that the fluctuation in the ratio with increasing concentration is much less than the

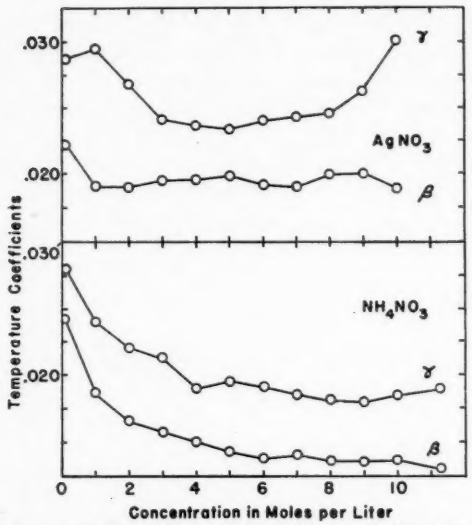

FIG. 3. Temperature coefficients of conductance (β) and fluidity (γ) vs. concentration.

TABLE II

TEMPERATURE COEFFICIENTS OF CONDUCTANCE AND FLUIDITY

Molarity	Absolute fluidity		Equivalent conductance		Coefficient of:		γ/β
	25°C.	95°C.	25°C.	95°C.	Fluidity γ	Conductance β	
A. Silver nitrate							
0.00	111.9	334.0	....	....	0.0283	....	....
0.1	110.9	334.0	109.1	278	0.0287	0.0222	1.39
1.0	104.2	318.1	77.8	182	0.0295	0.019	1.55
2.0	94.9	272.7	64.2	151	0.0268	0.019	1.41
3.0	85.6	230.3	55.0	130	0.0242	0.0195	1.24
4.0	76.0	202.4	48.5	116	0.0237	0.0195	1.22
5.0	67.6	178.1	43.1	101.5	0.0234	0.0198	1.18
6.0	59.2	159.0	38.6	90.0	0.0241	0.0191	1.26
7.0	51.6	139.2	34.7	81.5	0.0243	0.0190	1.27
8.0	44.7	121.5	31.2	74.0	0.0246	0.0198	1.24
9.0	37.3	106.0	28.3	67.0	0.0263	0.0199	1.31
10.0	32.2	92.8	26.1	60.0	0.0313	0.0187	1.67
B. Ammonium nitrate							
0.00	111.9	334.0	....	....	0.0283	....	....
0.100	112.9	330.7	112.95	306.0	0.0275	0.0244	1.13
1.004	116.5	312.1	101.32	234.0	0.0240	0.0187	1.28
1.993	117.6	300.9	91.95	199.7	0.0222	0.0167	1.33
2.982	114.5	285.4	84.28	177.3	0.0214	0.0158	1.35
4.020	110.9	269.4	76.78	158.0	0.0190	0.0151	1.26
5.014	105.4	249.2	70.00	140.5	0.0195	0.0144	1.35
6.036	97.81	228.8	63.12	124.5	0.0192	0.0139	1.38
7.015	90.7	207.4	56.73	110.5	0.0185	0.0136	1.36
8.011	81.9	186.5	50.36	97.4	0.0182	0.0133	1.37
9.043	73.1	164.5	43.93	84.5	0.0179	0.0132	1.36
10.004	63.0	145.2	38.19	73.8	0.0186	0.0133	1.40
11.282	51.6	120.1	31.3	60.2	0.0190	0.0132	1.44

progressive changes in γ and β individually; (these tend on the whole to decrease). The ratio shows an increase, if anything, but the deviations from constancy are no greater than might be due to our gross assumptions of linear temperature relations for fluidity and conductance. It is also true that our determinations of fluidity do not possess the high accuracy of our conductance measurements. It is our intention in the immediate future to determine densities, viscosities, and conductances at 10 degree intervals, between 25° and 95°, and evaluate the constants of the virial and exponential equations, and in this way perhaps demonstrate either a greater constancy or the true relation between the temperature coefficients of fluidity and of conductance.

In the case of certain electrolytes, particularly in nonaqueous solutions, the product of equivalent conductance and absolute viscosity remains constant with varying concentration and with varying temperature. This expression has been evaluated for silver nitrate and for ammonium nitrate at 25° and 95°, and for acetic acid at 25°, all over the high concentration range (Table III).

TABLE III

THE PRODUCT $\Lambda\eta$ (η = ABSOLUTE VISCOSITY)

A. Silver nitrate				B. Ammonium nitrate			C. Acetic acid	
Molarity	$\Lambda\eta$ at 25°C.	Molarity	$\Lambda\eta$ at 95°C.	Molarity	$\Lambda\eta$ at 25°C.	$\Lambda\eta$ at 95°C.	Molarity	$\Lambda\eta$ at 25°C.
0.100	0.9838	0.1	0.8323	0.100	1.001	0.925	1.735	0.0108
1.074	0.7469	1.0	0.5722	1.004	0.8693	0.750	3.437	0.00668
1.998	0.6767	2.0	0.5537	1.993	0.7823	0.664	5.206	0.00453
3.028	0.6420	3.0	0.5645	2.982	0.7258	0.621	6.751	0.00318
4.000	0.6383	4.0	0.5730	4.020	0.6924	0.586	8.423	0.00182
5.029	0.6393	5.0	0.5698	5.014	0.6637	0.564	10.106	0.00123
6.006	0.6511	6.0	0.5658	6.036	0.6453	0.544	11.883	0.00062
7.012	0.6714	7.0	0.5856	7.015	0.6256	0.533	13.585	0.00042
8.011	0.6986	8.0	0.6092	8.011	0.6147	0.522	15.415	7.77×10^{-4}
9.043	0.7499	9.0	0.6319	9.043	0.6011	0.514	17.36	4.50×10^{-4}
9.709	0.7769	10.0	0.6468	10.004	0.6062	0.503	....	....
....	....	....	....	11.283	0.6070	0.501	....	....

Over a range from 1 to 9 molar, the product at 95° for silver nitrate is 0.58 ± 0.05—remarkable constancy considering the large change in conductance and viscosity over this range (Λ varies from 172 to 40 mhos and η from 1.1 to 4.3 (relative viscosity)). Similar results are obtained at 25°. In the case of ammonium nitrate the constancy is not so striking, the product dropping continuously from 0.75 at 1 molar and appearing to level off at 0.50 for 11.3 molar. Over this range the conductance changes from 235 to 30 mhos and η from 1.05 to 4.29. This again emphasizes the fact that fluidity is not the sole determining factor in the effect of temperature on conductance. It is interesting to note that the product for acetic acid varies 10-fold over a similar concentration range.

The partial molar volumes of water in these solutions have been evaluated by the usual methods, using our density figures. The partial molar volume of water in silver nitrate solutions drops progressively from 18.75 ml. at 0.02

mole fraction silver nitrate to 16.65 ml. at 0.36 mole fraction, while for ammonium nitrate the partial molar volume appears to decrease from 18.73 ml. at 0.016 mole fraction to a minimum of 17.75 ml. at 0.34 mole fraction and then to increase to 20.3 ml. at 0.57 mole fraction. Because of the large effect on the partial molar volume of small errors in density in this region we intend to accumulate further experimental data before claiming an actual expansion or increase in the partial molar volume of water.

CONCLUSIONS

Despite the fact that our measurements of conductance at 95° of solutions of silver nitrate and of ammonium nitrate have now been pushed to mole fractions 0.36 and 0.57 respectively, the equivalent conductance continues to decrease along a smooth curve. The linear relation between Λ and C is very interesting. Although fluidity is certainly a factor in the increase of conductance with temperature, our results show that it is not the sole factor. We think that it is possible that there is a constant ratio between the coefficients of fluidity and of conductance and, if so, this points to a relatively simple explanation for the increase of conductance with temperature.

ACKNOWLEDGMENT

We are indebted to the National Research Council for grants which have defrayed most of the expense of this investigation.

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ISOTOPE EFFECTS IN THE THERMAL DEAMMONATION OF PHTHALAMIDE[1]

By F. W. Stacey,[2] J. G. Lindsay,[3] and A. N. Bourns

ABSTRACT

A study has been made of the nitrogen isotope effects occurring in the deammonation of phthalamide of normal isotopic abundance. It has been found that the reaction of phthalamide-$N^{14}N^{15}$ leading to $N^{14}H_3$ formation occurs 1.2% more readily than that giving $N^{15}H_3$. In addition, a 0.6% greater probability of formation of $N^{14}H_3$ from phthalamide-N^{14},N^{15} than from phthalamide-N^{14},N^{14} has been observed, due consideration being given to the presence of one N^{14} atom in the former and two N^{14} atoms in the latter amide species. An explanation has been advanced based on the effect upon activation energy of the isotopic mass of the nitrogen atom in the C–N bonds broken and formed in the reaction.

INTRODUCTION

Although isotope effects in unidirectional processes involving deuterium have been known for some time, it has only been in the last few years that effects of appreciable magnitude have been demonstrated in reactions involving compounds containing isotopic atoms of higher atomic weight, namely, C^{13}, C^{14}, N^{15}, and O^{18}. The carbon isotope effect in the decarboxylation of malonic acid has received the greatest attention. Yankwich and Calvin (12) studied the decarboxylation of malonic acid containing C^{14} in one carboxyl group and reported that the ratio of the frequency of rupture of a C^{12}–C^{12} bond to that of a C^{12}–C^{14} bond in the labeled acid was 1.12 ± 0.03, which represents an isotope effect of 12%. Bigeleisen and Friedman (3), using normal malonic acid, obtained a smaller effect (2%) than would be expected on the assumption that the effect with C^{13} should be half that with C^{14}. This experimental value was in close agreement with the theoretical value calculated by these authors. Lindsay, Bourns, and Thode (7), working in this laboratory with normal malonic acid, obtained a 2% effect, thus confirming Bigeleisen's value, while very recently Roe and Hellman (11) have repeated the decarboxylation studies using malonic-1-C^{14} acid and found a $6\pm2\%$ effect. This latter value is considerably smaller than that reported by Yankwich and Calvin for the C^{14} acid and approaches the theoretical value of 4%. In addition to this so-called intramolecular isotope effect, a second, or intermolecular, isotope effect has been determined. This may be expressed as the ratio of the rate of formation of $C^{12}O_2$ from malonic acid containing only C^{12} atoms to twice the rate of formation of $C^{13}O_2$ from the acid containing a C^{13} atom in one carboxyl group. Bigeleisen and Friedman (3) have reported this ratio as 1.037 while Lindsay, Bourns, and Thode (7) have published a value of 1.046.* An

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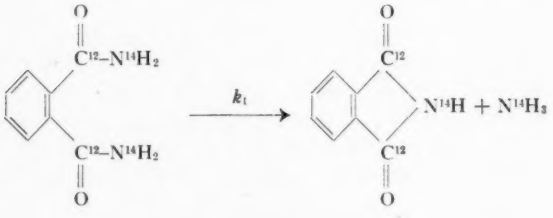
* *A value of 1.036 for this ratio has been found in more recent work in this laboratory.*

isotope effect of approximately the same magnitude has recently been reported in the decarboxylation of normal mesitoic acid (4) and normal trichloroacetate ion (2). These findings have led Bigeleisen to conclude that the isotope effect is not affected appreciably by the nature of the acid studied or by the medium.

Considerably less work has been reported on isotope effects in which carbon-to-nitrogen or oxygen-to-nitrogen bonds are involved. Myerson and Daniels (8) have found that during the enzymatic hydrolysis of C^{14} labeled urea, the carbon dioxide produced early in the reaction had a higher specific activity than that produced later in the hydrolysis. This would indicate that, contrary to expectation, molecules containing the heavier carbon isotope are the more readily hydrolyzed. Recently Friedman and Bigeleisen (6) have reported the results of a very careful study of the oxygen and nitrogen isotope effects in the decomposition of ammonium nitrate. They found that the N_2O formed during 1% decomposition was enriched in N^{14} but that the ratio of the oxygen isotopes in this sample was the same as in the N_2O formed by complete decomposition of the ammonium nitrate. It was further found, in the complete decomposition, that the O^{18} content of the N_2O was greater than that of the H_2O suggesting that $N–O^{16}$ bonds break preferentially to $N–O^{18}$ bonds.

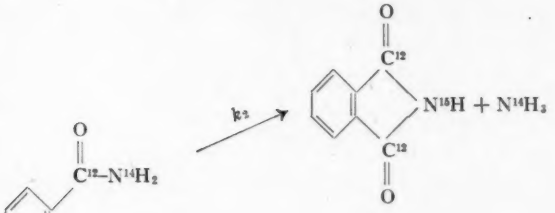
This paper reports the results of a study of the effect of isotopic mass of the nitrogen atom on the rate of decomposition of phthalamide of normal N^{15} content to phthalimide and ammonia. Two isotope effects have been determined, one providing a measure of the relative rates of splitting of a $C^{12}–N^{14}$ bond and $C^{12}–N^{15}$ bond in a phthalamide molecule containing one N^{15} atom only, and the second giving the relative rates of formation of $N^{14}H_3$ from phthalamide-N^{14},N^{14} and $N^{15}H_3$ from phthalamide-N^{14},N^{15}, due consideration being given to the fact that the latter molecule contains only one N^{15} atom.

The decomposition of phthalamide (N^{15} content approximately 0.4%) may be represented by the following equations where k_1, k_2, and k_3 represent specific reaction rate constants:*

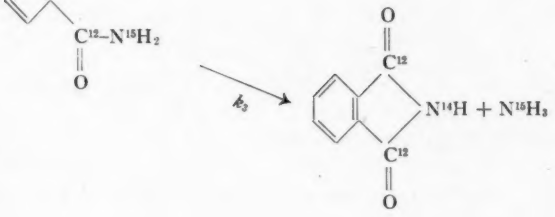


(1)

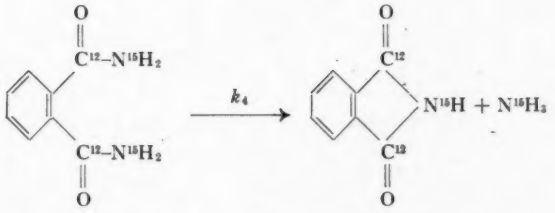
* *It may be readily shown that any error introduced by neglecting those species of molecules containing one or two C^{13} carboxyl atoms is considerably smaller than the experimental error involved in the mass spectrometer measurements.*



(2)



(2′)



(3)

The reaction was found to be of first order.* Therefore, at any time t

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{M_1^0(1 - e^{-k_1 t}) + \frac{k_2}{k_2 + k_3} M_2^0(1 - e^{-(k_2+k_3)t})}{\frac{k_3}{k_2 + k_3} M_2^0(1 - e^{-(k_2+k_3)t}) + M_3^0(1 - e^{-k_4 t})} \tag{4}$$

where M_1^0, M_2^0, and M_3^0 are the mole fractions of the different isotopic species of phthalamide in Equations 1, 2, 2′, and 3, respectively. When $t = \infty$, Equation (4) becomes

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{M_1^0 + \frac{k_2}{k_2 + k_3} M_2^0}{M_3^0 + \frac{k_3}{k_2 + k_3} M_2^0}. \tag{5}$$

When t is small (4) becomes

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{k_1 M_1^0 + k_2 M_2^0}{k_3 M_2^0 + k_4 M_3^0}. \tag{6}$$

* *The order of the deammonation reaction was determined by decomposing phthalamide at 210°C. and measuring the rate of formation of ammonia. The specific reaction rate constant for the reaction at this temperature was 3.6 × 10⁻² sec.⁻¹*

Letting a be the atom fraction N^{15} occurring in the normal phthalamide, it follows that

$$M_1^0 = (1 - a)^2$$
$$M_2^0 = 2a(1 - a)$$
$$M_3^0 = a^2 .$$

Substituting these values in Equations (5) and (6) we obtain the following: at $t = \infty$

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{(1 - a)^2 + \frac{k_2}{k_2 + k_3}[2a(1 - a)]}{a^2 + \frac{k_3}{k_2 + k_3}[2a(1 - a)]} \tag{7}$$

which may be converted into the form

$$\frac{k_2}{k_3} = \frac{a(2 - a) - \left[\frac{N^{15}H_3}{N^{14}H_3}\right](1 - a)^2}{\left[\frac{N^{15}H_3}{N^{14}H_3}\right](1 - a^2) - a^2} \tag{7'}$$

and at t small

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{k_1(1 - a)^2 + 2k_2a(1 - a)}{2k_3a(1 - a) + k_4a^2} \tag{8}$$

which, after making the approximations $k_1 \doteq 2k_2$ and $k_4 \doteq 2k_3$, may be converted into the form

$$\frac{k_1}{2k_3} = \left[\frac{N^{14}H_3}{N^{15}H_3}\right]\frac{a}{1 - a} . \tag{8'}$$

The value of a is obtained by a mass spectrometric analysis of the nitrogen gas formed by the oxidation of the ammonia which is produced by the complete hydrolysis of phthalamide. The ratio, $\frac{N^{15}H_3}{N^{14}H_3}$, in Equation (7′) is obtained by analysis of the nitrogen prepared from the ammonia produced by the complete thermal deammonation of phthalamide, while this ratio for Equation (8′) is obtained by a similar determination of the ratio of the nitrogen isotopes in the first small amount of ammonia evolved from the thermal decomposition of a relatively large sample of the amide. In this manner, the ratio, $\frac{k_2}{k_3}$, giving the relative rates of the reactions involving the breaking of a C^{12}–N^{14} bond and a C^{12}–N^{15} bond in phthalamide-N^{14},N^{15}, may be calculated from Equation (7′). The ratio, $\frac{k_1}{2k_3}$, obtained from equation (8′), gives the ratio of the rate of formation of $N^{14}H_3$ from phthalamide-N^{14},N^{14} to twice the rate of formation of $N^{15}H_3$ from phthalamide-N^{14},N^{15}.

The same rate-constant ratios may be equally well determined by using

the ratios of the nitrogen isotopes in the other product of the deammonation reaction, namely, phthalimide. The nitrogen of the phthalimide is converted into ammonia by hydrolysis and oxidized to nitrogen gas for mass spectrometric analysis.

EXPERIMENTAL

The phthalamide used in all experiments was a B.D.H.—Certified Chemical grade, m.p. 222-223°C. Calc. for $C_8H_8O_2N_2$: N, 17.07%. Found (Kjeldahl): N, 17.0, 16.9, 17.0. Purification by crystallization was not successful and the commercial product was used without further treatment.

The deammonations were carried out in a small test-tube shaped reactor at temperatures regulated to within one degree centigrade. The ammonia produced was carried by means of a slow stream of purified hydrogen into excess 0.1*M* hydrochloric acid. The phthalimide formed during the decomposition sublimed to the cold upper part of the reaction tube. In the experiments in which the reaction was carried to completion, 200 mgm. of the amide was heated at the desired temperature until all of the compound had disappeared from the bottom of the reactor. The sublimate was then pushed down and the heating continued until it had again sublimed to the top of the tube. The yield of ammonia was determined in every case and only those samples which were produced from experiments in which the yield exceeded 90% were prepared for analysis. The failure to obtain quantitative yields of ammonia appeared to be due to the sublimation of a small amount of amide during the deammonation reaction since the hydrolysis of the phthalimide gave slightly more than the theoretical amount of ammonia. This would suggest some contamination by a compound of higher nitrogen content. Resublimation of the phthalimide failed to remove this impurity.

Five-gram samples of phthalamide were used in experiments involving the determination of the rate-constant ratio $\frac{k_1}{2k_3}$ and the first 2% of the ammonia produced was collected in an equivalent amount of standard hydrochloric acid using methyl red as the indicator. The imide was not recovered in these experiments.

Hydrolysis of both phthalamide and phthalimide was effected by refluxing 100 mgm. of the compound with 15 ml. of 10% sodium hydroxide, and the ammonia so produced was carried by means of a stream of purified hydrogen into excess 0.1*M* hydrochloric acid. Yields of ammonia from phthalamide were quantitative, and 2 to 5% above theoretical in the case of the imide.

The ammonia samples were oxidized quantitatively to nitrogen by sodium hypobromite in a high-vacuum system according to the procedure developed by Rittenberg (10). Sufficient ammonia was oxidized to produce a pressure of nitrogen equivalent to 20 – 25 cm. of mercury in a sample tube of 10 – 15 ml. capacity.

Mass Spectrometer Analyses

All nitrogen samples were analyzed in a 180° direction focusing mass spectrometer using an automatic recorder. The ratio of mass 28 to 29, $\frac{N^{14}N^{14}}{N^{15}N^{14}}$, of each nitrogen sample was measured relative to a standard, this being a sample of purified tank nitrogen. The absolute value of the $\frac{N^{14}N^{14}}{N^{15}N^{14}}$ ratio of the standard varied somewhat from day to day and therefore to permit comparisons between samples it was necessary to assign an arbitrary value for this ratio of the standard and to normalize all sample ratios to this value. The ratio chosen for the standard was 136.20. The procedure was to analyze the standard, the sample, and the standard again in that order with as little delay between samples as possible. An analysis was considered satisfactory only if the two standards checked to within 0.1%, the precision of a single analysis. Automatic magnetic scanning was used throughout. A single analysis consisted of six or seven spectrograms, each spectrogram consisting of masses 28 and 29 and then by reversing the direction of scan, masses 29 and 28.

RESULTS AND DISCUSSION

The results of the deammonation experiments in which the reaction was taken to completion are given in Table I. It is seen that a value of 1.014± 0.001 for the ratio $\frac{k_2}{k_3}$ was obtained using the ratio of the nitrogen isotopes

TABLE I

COMPLETE DECOMPOSITION REACTIONS AT 180°C.*

Expt.	N_2^{28}/N_2^{29} ratio**		k_2/k_3 calculated from:	
	Ammonia	Imide	Ammonia	Imide
D–H–1	135.47 ± 0.08	134.23 ± 0.04	1.009	1.009
D–H–3	135.81 ± 0.11	134.28 ± 0.05	1.015	1.008
D–H–7	135.77 ± 0.07	133.96 ± 0.10	1.014	1.013
D–H–10	135.92 ± 0.08		1.016	
D–H–11	135.77 ± 0.07	134.18 ± 0.09	1.014	1.010
D–H–12	135.86 ± 0.08		1.015	
		Mean	1.014 ±.001	1.010 ±.001

* *All precisions are expressed in terms of average deviation of the mean.*
** *The N_2^{28}/N_2^{29} ratio for phthalamide was 134.83.*

in the ammonia produced and a value of 1.010±0.001 from the ratio of the nitrogen isotopes in phthalimide. The former may be more reliable since, as discussed in the previous section, the imide product appeared to be slightly contaminated with unchanged reactant. It is apparent from these results that of the two modes of decomposition of phthalamide-N^{14},N^{15} the one involving the rupture of a C^{12}–N^{14} bond occurs preferentially. This is consistent with the results of the malonic acid decarboxylation studies in which the relative

rates of rupture of C^{12}–C^{12} and C^{12}–C^{13} bonds in malonic-1-C^{13} acid were determined (3, 7).

The results obtained from the partial decomposition of phthalamide are given in Table II. The experimentally determined rate-constant ratio is $\frac{k_1}{2k_3}$, for which the value 1.006 ± 0.001 was obtained. Combination of this value with the value obtained for the ratio $\frac{k_2}{k_3}$ permits the calculation of the ratios $\frac{k_1}{2k_2}$ and $\frac{k_1}{k_2 + k_3}$. The ratio $\frac{k_1}{2k_3}$ is a measure of the rate of deammonation of phthalamide-N^{14},N^{14} relative to that reaction of phthalamide-N^{14},N^{15} in which $N^{15}H_3$ is produced, while $\frac{k_1}{2k_2}$ measures the rate of reaction involving

TABLE II

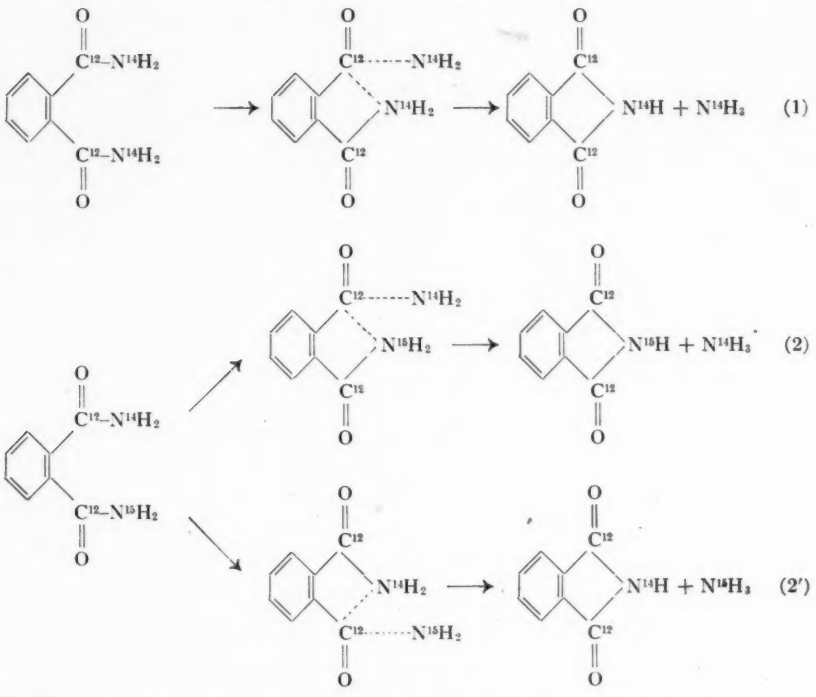
PARTIAL DECOMPOSITION REACTIONS*

Expt.	Temp., °C.	N_2^{28}/N_2^{29} ratio **, ammonia	$k_1/2k_2$	$k_1/2k_3$	k_1/k_2+k_3
101	180	135.48 ± 0.03	0.993	1.005	0.999
103	180	135.88 ± 0.09	0.996	1.008	1.002
104	180	135.51 ± 0.06	0.993	1.005	0.999
105	180	135.57 ± 0.05	0.994	1.006	1.000
106	180	135.66 ± 0.05	0.994	1.006	1.000
107	190	135.60 ± 0.05	0.994	1.006	1.000
108	210	135.85 ± 0.08	0.996	1.008	1.002
		Mean ***	0.994 ±.001	1.006 ±.001	1.000 ±.001

* *All precisions are expressed in terms of average deviation of the mean.*
***The N_2^{28}/N_2^{29} ratio for phthalamide was 134.83.*
*** *The absence of an appreciable temperature coefficient provides justification for taking a mean of results obtained at different temperatures.*

phthalamide-N^{14},N^{14} relative to that reaction of phthalamide-N^{14},N^{15} leading to $N^{14}H_3$ formation. The ratio $\frac{k_1}{k_2 + k_3}$ gives the relative rates of reaction of the two amide species, phthalamide-N^{14},N^{14} and phthalamide-N^{14},N^{15}. The value for $\frac{k_1}{k_2 + k_3}$ of unity and for $\frac{k_1}{2k_2}$ less than unity would appear to be at variance with the malonic acid results in which rate-constant ratios for analogous isotopic reactions were found in each case to be greater than unity.

A possible explanation of the phthalamide results may be found by a consideration of the mechanism of the deammonation reaction. This may reasonably be pictured as being analogous to the simple three centre displacement reaction of the type: $A + B - C \rightarrow A\text{---}B\text{---}C \rightarrow A - B + C$, where A---B---C represents the activated complex. The deammonation reaction, then, may be represented as follows—



It can be seen that Reaction (1) involves the rupture of a C^{12}–N^{14} bond with the simultaneous formation of a new C^{12}–N^{14} bond, while Reaction (2) involves the rupture of a C^{12}–N^{14} bond together with the formation of a C^{12}–N^{15} bond. The two reactions differ only in respect to the isotopic mass of the nitrogen atom in the bond which is formed. Reactions (1) and (2′), on the other hand, differ in respect to the bond which is broken but are identical in the bond which is formed. Finally, Reactions (2) and (2′) differ both in respect to the bond broken and the bond formed.

Theoretical considerations (1) as well as experimental results in previous studies of isotope effects (2, 3, 4, 7, 11) have established that the substitution of a heavier for a lighter isotope in a bond results in a higher energy of activation for the reaction in which the bond in question is undergoing fission. It follows that, on the basis of bond rupture alone, the reaction of phthalamide in which C^{12}–N^{14} bond rupture is involved should proceed more readily than that in which a C^{12}–N^{15} bond is broken. The energy of activation, however, will also be influenced by the energies of the products since in the transition state the interacting system has begun to assume the configuration of the products (5, 9). Therefore two final states of slightly different energy will be represented in the activated complex as different energy levels. In the case in point, the product phthalimide-N^{15} will have a lower total zero

point energy than the product phthalimide-N^{14}. Hence, other things being equal, that reaction involving the formation of a C^{12}–N^{15} bond will require a lower activation energy, and proceed more rapidly, than the reaction in which a C^{12}–N^{14} bond is formed. It follows, then, that in order to arrive at any conclusion concerning the relative rates of the three reactions of phthalamide given above it is necessary to consider the isotopic nature both of the bonds broken and of the bonds formed in the deammonation process. The case of phthalamide is unique among the "isotope effect" researches studied to date in that the bond which is starting to form in the transition state involves the same kind of atoms, namely, carbon and nitrogen, as the bond which at the same time is starting to break.

Referring to the Reactions (1), (2), and (2′) given above, it is apparent that the lowest activation energy will be required for Reaction (2) since, in this case, the bond, C^{12}–N^{14}, involving the lighter nitrogen isotope is broken and the bond, C^{12}–N^{15}, containing the heavier isotope is formed. Reaction (2′), on

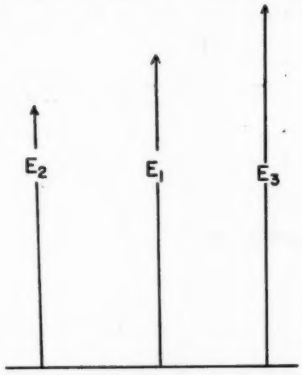


FIG. 1. Relative activation energies.

the other hand, will require the greatest activation energy since a C^{12}–N^{15} bond is broken and a C^{12}–N^{14} bond is formed. Finally Reaction (1), involving as it does the rupture and formation of C^{12}–N^{14} bonds will require an activation energy intermediate between that of Reactions (2) and (2′). This is shown diagrammatically in Fig. 1 in which E_1, E_2, and E_3 are the energies of activation of Reactions (1), (2), and (2′), respectively.

The rate-constant ratio $\frac{k_2}{k_3}$ will be given by the expression, $\frac{k_2}{k_3} = e^{\frac{-(E_2 - E_3)}{RT}}$, and since E_3 is greater than E_2 this ratio will be greater than unity. The ratio $\frac{k_1}{2k_2}$ will be less than unity since it is given by the expression, $\frac{k_1}{2k_2} = e^{\frac{-(E_1 - E_2)}{RT}}$, in which E_1 is greater than E_2. Finally, $\frac{k_1}{2k_3}$ is given by the expression, $\frac{k_1}{2k_3} = \frac{-(E_1 - E_3)}{RT}$, and will have a value greater than one. Furthermore if the assumption is made that the influence upon activation energy of the iso-

topic mass of nitrogen is approximately the same in bond rupture and in bond formation, it follows that

$$(E_2-E_3) \simeq 2(E_1-E_3) \simeq -2(E_1-E_2).$$

The exponential terms being small, the difference from unity of the three rate constants, i.e., the isotope effects, will be related to each other in the following way:

$$\frac{k_2}{k_3} - 1 \simeq 2\left(\frac{k_1}{2k_3} - 1\right) \simeq 2\left(1 - \frac{k_1}{2k_2}\right).$$

The results reported in Tables I and II are in accord with these considerations.

In this discussion, the assumption has been made that the reacting species, both in the initial and transition state, are in their lowest energy levels. This has simplified the treatment to the extent that partition function ratios do not appear in the expressions relating rate constant ratios to differences in activation energy. Actually, energy levels other than the lowest will also be populated. However, the argument given above should still be valid, since it

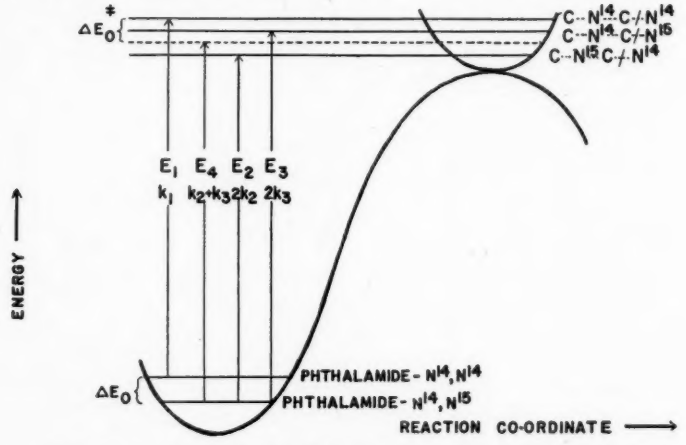


FIG. 2. Relative energy levels in reactants and activated complex.

is reasonable to assume that under the conditions of the reaction the lowest levels will be the most heavily populated.

It is of interest to extend the argument to a consideration of the relative positions of the zero point energy levels of the two species, phthalamide-N^{14},N^{14} and phthalamide-N^{14},N^{15}, in the initial state and in the activated complex. This is shown diagrammatically in Fig. 2. Two levels exist in the initial state, one for each of the two isotopic species. Since the over-all zero point energy of phthalamide-N^{14},N^{15} will be less than that of phthalamide-N^{14},N^{14}, the former will occupy the lower energy level. In assigning but one level to phthalamide-N^{14},N^{15} in the initial state the assumption is here implied that the molecule as a whole is activated and not a particular bond. This appears valid since there

can be but one partition function for this molecular species regardless of the configuration that it may assume in the transition state.

Turning to the transition state, two energy levels are assigned to the species, phthalamide-N^{14},N^{15}, one for the configuration leading to phthalimide-N^{15} and the other to phthalimide-N^{14}. The former will possess the lower energy since it has been formed by the partial rupture of a C^{12}–N^{14} bond and partial formation of a C^{12}–N^{15} bond. There is but one energy level for the activated phthalamide-N^{14},N^{14} molecule and its position, relative to levels for phthalamide-N^{14},N^{15}, can not be definitely assigned. However, since $E_1 \doteq \frac{E_2+E_3}{2}$ (Fig. 1), it follows that the difference ($\Delta E_0^{\ddagger}$) in zero point energy between the activated phthalamide-N^{14},N^{14} level and the mean of the two levels for activated phthalamide-N^{14},N^{15} is equal to the difference (ΔE_0) in zero point energy of the two isotopic species in their initial states. Depending upon the magnitude of ΔE_0 as compared to the difference in energy between the mean of the two levels for the activated phthalamide-N^{14},N^{15} molecule and the higher level for this species, the activated phthalamide-N^{14},N^{14} level may be above or below this higher level.

It will be noted that isotope effects arising from the rupture and formation of N–H bonds have been ignored. These effects presumably will operate in opposition to the effects arising from C–N bond rupture and formation. Calculations have indicated, however, that the magnitude of the nitrogen isotope effects in N–H bonds is considerably less than the effects arising from C–N bonds and therefore in the present discussion may be neglected without effecting the validity of the argument.

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RADIOCHEMICAL MEASUREMENTS OF ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTES[1]

By R. H. Betts and Agnes N. MacKenzie

ABSTRACT

A method is described for the precise measurement of the activity coefficients of salts in mixed electrolytic solutions. It involves the use of synthetic ion exchange resins and radioactive tracers. The activity coefficients of the chlorides of sodium, potassium, rubidium, and cesium were measured at effectively zero concentration in hydrochloric acid solutions from 0.005 to 1.5 *m*. The activity coefficient of sodium chloride in solutions of lithium and potassium chlorides was also determined. The results are discussed in terms of both the Harned rule and the Stokes–Robinson theory of activity coefficients.

INTRODUCTION

The practical activity coefficient γ of an electrolyte dissolved in aqueous solution is defined as the ratio of the mean activity of the electrolyte to its mean molality (8, p.10). Much information, both experimental and theoretical, is available regarding this important quantity for single electrolytes in pure solution. However only scanty data are available relating to the activity coefficient of electrolytes in the presence of co-solutes. Such solutions are of considerable interest, since the majority of chemical reactions and equilibria in aqueous solutions involve at least two components, in addition to the solvent.

Two principal methods have been used in the past to investigate activity coefficients of individual electrolytes in mixed electrolytic solutions. The first of these involves the measurement of the solubility of slightly soluble compounds in the presence of added electrolytes (8, p.445). This method suffers from an obvious limitation, in that one component of the solution should be relatively insoluble in the presence of the other component. The second method, developed by Harned, depends on the measurement of the electromotive force of suitable reversible cells (8, p.450). This procedure is limited to the investigation of the activity coefficients of acids or bases in the presence of dissolved salts. In certain cases, it is possible to measure the activity coefficients of both salt and base in the same solution, e.g., the systems sodium hydroxide – sodium chloride and potassium hydroxide – potassium chloride have been studied in this way (8, p.474). These experiments are among the few systematic studies ever reported in which the activity coefficients of *both* the electrolytic components were measured.

Schubert (13) has described recently a radiochemical method for the determination of activity coefficients of electrolytes at low concentrations in the presence of other electrolytes at higher concentration. We shall consider in this paper how these radiochemical procedures may be used to verify some of the predictions arising from Harned's investigations, notably that there exists a predictable linear relation between the logarithm of the activity coefficient of the salt and its molality in hydrochloric acid solutions (8, p.459). For this

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purpose, we have measured the activity coefficients of the chlorides of sodium, potassium, rubidium, and cesium at essentially zero concentration in hydrochloric acid solutions. In addition, we report experiments relating to the activity coefficient of sodium chloride in the presence of potassium and lithium chlorides as co-solutes. The latter results cannot be used to verify Harned's rule, since the behavior of neither component in the presence of the other is known from separate experiments. However, we shall discuss these results together with the rest in terms of the recently proposed hydration theory of activity coefficients (17).

The radiochemical method used in this investigation involves the measurement of the distribution of a suitable radiotracer between a given solution and a synthetic ion exchange resin like Dowex 50 (13). To illustrate the method, we shall consider its application to the system hydrochloric acid – sodium chloride, with the understanding that similar discussion applies to the other systems as well. If the hydrogen form, designated as HR, is equilibrated with an aqueous solution of hydrochloric acid and sodium chloride, equilibrium is soon established for these species between the two phases:

(1) $$HR + Na^+ \rightleftharpoons NaR + H^+.$$

The exact mechanism of the exchange is still somewhat obscure (4,11) but regardless of what theory is used, for uni-univalent electrolytes of the type under discussion, a Mass Action expression governs the position of equilibrium:

(2) $$K_a = g.\ \frac{(NaR)\ [H^+]\ \gamma_{H+}}{(HR)\ [Na^+]\ \gamma_{Na+}}.$$

K_a is the thermodynamic equilibrium constant. The square brackets denote molal concentrations of the enclosed species, and the γ terms are the corresponding ionic activity coefficients. It is more useful to transform Equation (2) to the form:

(3) $$K_a = g.\ \frac{(NaR)\ [H^+]\ \gamma_{H+}}{(HR)\ [Na^+]\ \gamma_{Na+}} \cdot \frac{[Cl^-]\ \gamma_{Cl^-}}{[Cl^-]\ \gamma_{Cl^-}} = g.\ \frac{(NaR)\ [H^+]\ \gamma^2_{HCl}}{(HR)\ [Na^+]\ \gamma^2_{NaCl}}$$

where the final γ terms are the practical activity coefficients of the indicated components *in the mixed electrolyte*. The curved brackets denote moles of the enclosed species. Other investigations have shown that the thermodynamic activities of the species in the resin phase are approximately proportional to the mole fraction of each component in that phase (4,5,11). For example, a recent paper has shown that for the system NaCl–HCl–HR, the ratio of the activity coefficients of the components *on the resin phase* is equal to unity for displacements of hydrogen ion varying from zero to 20% (1). The factor g is introduced as an empirical parameter to take account of any possible departures from unity in this ratio.

Setting aside for the moment possible complications due to variations in g, if values of γ_{HCl} and γ_{NaCl} for the mixed electrolyte are known, it is possible to evaluate K_a for a resin by measurement of the distribution of the two species between the resin and the solution. In dilute solution, e.g. 0.005 m hydrochloric acid and 10^{-6} m sodium chloride, the activity coefficient of each species

will be determined almost exclusively by the ionic strength of the medium; the Lewis rule (10, p. 374), supported by the Debye–Hückel theory, may be applied, i.e., the activity coefficient of a given valence type of electrolyte will be the same in all solutions of the same ionic strength. Accordingly *for these conditions*, $\gamma_{NaCl} = \gamma_{HCl}$, and hence measurement of the concentration ratios indicated in Equation (3) gives directly K_a for the resin.

For solutions of higher concentrations of hydrochloric acid, but still containing sodium chloride at very low concentration, it is permissible to equate the activity coefficient of the acid in the mixed electrolyte to its value in pure solution at the same ionic strength. Hence measurement of the distribution ratios, together with a knowledge of K_a and γ_{HCl}, permits calculation of γ_{NaCl} at effectively zero concentration in the presence of hydrochloric acid.

We consider now the experimental criteria necessary to show whether the parameter g remains unchanged over a definite range in the mole ratio NaR/HR. By using 10^{-6} and 10^{-5} m sodium chloride solutions, it is possible to vary this ratio by a factor of 10 without otherwise changing the experimental conditions. If K_a determined over this range of concentrations is constant, one may conclude that the factor g has remained unchanged. By appropriate choice of conditions, all subsequent experiments at other concentrations of hydrochloric acid may be arranged to give values of the mole ratio NaR/HR within the limits for which the behavior of the parameter g is known. In this way, variations in measured K_a values may then be attributed with certainty to variations in the term γ^2_{NaCl}, and not to changes in g.

It is convenient now to develop a general form of Equation (3) which may be applied directly to the experimental data. Since the concentration of the major electrolytic component BCl will be several orders of magnitude greater than that of the trace electrolyte MCl, the contribution of the latter to the composition and density of the solution may be neglected.

Let a = grams of air-dried resin BR in the system and

b = grams of solution of BCl of molality m and density D grams per ml.

Let c = the counts per minute (c.p.m.) per mole of trace electrolyte MCl. Since this term will cancel in the following derivation, it is unnecessary to know its value. It is introduced merely to clarify the presentation.

Let d/e = ratio of c.p.m. of radiotracer per gram of resin at equilibrium, to c.p.m. of radiotracer per gram of solution,

k = capacity of the resin, in units of equivalents per gram.

Provided the displacement of the ion originally on the resin is negligible, then at equilibrium:

$$(BR) = ka \text{ moles}, \tag{4}$$

$$(MR) = \frac{da}{c} \text{ moles}, \tag{5}$$

$$\text{and} \quad [M^+] = \frac{10^6 De}{c(1000D - W_{BCl}M)}. \tag{6}$$

The symbol M in Equation (6) refers to the molarity of electrolyte BCl at 25.0°C. corresponding to molality m. W_{BCl} is the molecular weight of BCl. Substitution of Equations (4), (5), and (6) into Equation (3) leads to:

$$K_a = \frac{dm}{10^6 ekD} \cdot (1000D - W_{BCl}M) \frac{\gamma^2_{BCl}}{\gamma^2_{MCl}}. \tag{7}$$

The terms in c cancel since in the present work the radioactive contents of the solution and the resin were determined by identical methods. For very dilute solutions of BCl, as we have seen, the activity coefficient terms cancel. Further, at very low molalities, the term $1000D$ is very much greater than $W_{BCl}M$ and hence K_a may be expressed as

$$K_a = \frac{d}{e} \cdot \frac{m}{10^3 k}. \tag{8}$$

Equation (8) gives an expression for K_a in terms of measurable quantities, i.e., the counting rate in solution and on the resin, the concentration of electrolyte BCl in solution, and the capacity of the resin.

At some other concentration of BCl m', where $m \ll m'$, it is necessary to use the extended expression for K_a:

$$K_a = \frac{d'}{e'} \cdot \frac{m'}{D'k10^6} \quad (1000D' - W_{BCl}M') \quad \frac{\gamma^2_{BCl}}{\gamma^2_{MCl}} \tag{9}$$

where the primed symbols refer to the corresponding quantities for this solution. Elimination of K_a between Equations (8) and (9) leads to the following as the expression for the activity coefficient of the trace electrolyte MCl, at effectively zero concentration, in the presence of electrolyte BCl at molality m':

$$\gamma_{MCl} = \gamma_{BCl} \sqrt{\frac{k\ m'\ \ d'e}{k\ m\ \ de'} \quad \frac{(1000D' - W_{BCl}M')}{10^3 D'}}. \tag{10}$$

Since the same batch of resin was used in all comparable experiments, the capacity terms k drop out of Equation (10).

The experimental work which follows describes the methods used to measure the ratio d/e, and hence the determination of the activity coefficient of the added metal chloride, as a function of the molality of the electrolyte BCl.

EXPERIMENTAL

Preparation of Materials

Solutions

All solutions were prepared from triply distilled water, containing less than 0.02 mgm. of dissolved solids per liter.

C.P. potassium chloride was further purified by three recrystallizations from water, followed by drying at 400°C. in platinum. Standard solutions were prepared from this material by weight.

A concentrated stock solution of lithium chloride was prepared by two recrystallizations of C.P. material from water. The purified stock solution was analyzed by conversion of weighed portions to anhydrous lithium sulphate

with sulphuric acid. Solutions of the desired concentration were prepared by weight from this standardized stock.

Aqueous solutions of hydrochloric acid were prepared from a concentrated stock solution, and standardized against sodium carbonate.

Preparation and Properties of the Ion-exchange Resins

The method described by Marinsky (11) was used to prepare the acid form of the resin. The initial material was 20–60 mesh size Nalcite HCR, a Dowex 50 type in the acid form. The resin was heated at about 80°C. for one day in 6 *M* sodium hydroxide to remove partially polymerized organic units, after which it was washed free of excess alkali, and reconverted to the acid form with 3*M* hydrochloric acid. The final washings and decantations to remove the excess acid were made with triply distilled water. This high quality water was used to ensure that no pickup of foreign ions occurred at this stage. It was then air-dried and finally stored in a glass-stoppered bottle. The lithium and potassium forms (LiR and KR) were made from the purified hydrogen resin by repeated contact with 3–4 *M* solutions of the corresponding chlorides. The complete replacement of hydrogen ion by lithium or by potassium was secured by addition of the appropriate alkali hydroxide to the solutions. These resins were then washed thoroughly with triply distilled water to free them from excess salt or base. After air-drying they were stored in glass-stoppered bottles.

The capacity of the hydrogen resin, determined by titration with standard alkali, was 4.12 m.e. of replaceable hydrogen-ion per gram of air-dried resin. The potassium resin was found to have a capacity of 3.98 m.e. per gram. The lithium resin was not analyzed for its lithium content. However on the basis of analysis of the sodium and potassium forms, which gave similar results, a value of 4.0 was assumed for the capacity of the lithium resin.

Preparation of Radioactive Tracers

The tracers used were Na^{24}, K^{42}, Rb^{86}, and 2.3 year Cs^{134}. They were prepared by neutron irradiation of very pure samples of the corresponding nitrates or carbonates in the NRX pile. After irradiation, the samples were converted to the chlorides by repeated evaporations with hydrochloric acid and finally dissolved in water. Measurements of the radioactive decay of the first two of these nuclides gave for the half-lives Na^{24}, 15.0 hr. and K^{42}, 12.3 hr., in good agreement with accepted values (16,14). Two separately prepared samples of Rb^{86} gave values of 18.7 and 18.5 days for the half-life. Values ranging from 18 to 19.5 days have been reported (15,9). Measurements of the radioactive decay of Cs^{134}, made after the 3.1 hour isomeric Cs^{134} had disappeared, indicated the absence of likely short-lived impurities, notably Na^{24}, Rb^{86}, and K^{42}. This nuclide was further characterized by comparison of the range in aluminum of its β-rays with those of UX_2 (1.14 minute Pa^{234}) by the method of Feather (7). These measurements gave 0.664 Mev. as the maximum energy for the β-rays of Cs^{134}. This agrees closely with a recently reported value of 0.658 Mev. (6).

Equilibration Procedure

The type of resin in each series of experiments was chosen to correspond with the electrolyte present in higher concentration, e.g., for HCl–Rb*Cl solutions, the acid form of the resin was used.

Mixtures for equilibration were prepared by weight in glass-stoppered flasks from the appropriate stock solutions and resins. The flasks were then shaken mechanically for two hours in a water bath maintained at 25.0°C. Separate experiments showed that equilibrium was reached in that time. Samples of the supernatant solution were then centrifuged to remove suspended particles of resin, and the radioactive content of the solution measured. Assay of the radioactive content of the original solution of tracer was made in the same way, except that no resin was present. Finally, the aqueous phase was analyzed for the concentration of the major electrolyte BCl. At least duplicate experiments were made for each concentration of BCl investigated.

Estimation of Radioactive Content of Solutions

Na^{24} was determined by measurement of the associated gamma-ray activity of weighed samples with a brass-walled Geiger counter. The details of the procedure have been described previously (3). The other radiotracers were measured by β–counting of samples with an end-on window Geiger counter and associated scaling circuit. Samples were prepared for counting by evaporation of weighed portions of solution on a well-defined central depression on a copper tray. The copper trays were of sufficient thickness to secure maximum, and therefore reproducible, back-scattering (18) from the most energetic β-rays emitted by K^{42} (3.57 Mev. (14)). Sufficient counts were recorded for each solution to reduce the so-called 9/10 statistical error to $\pm$ 0.3%.

Corrections were made in all cases for coincidence losses, background counts, and radioactive decay of the samples. In this connection, it is perhaps worthwhile to record that all samples in a given experiment were prepared so that each had approximately the same counting rate. Such a procedure minimized errors introduced because of uncertainties in the exact value of the resolving time of the counters. In addition, all samples to be compared were measured during an elapsed time of not more than four hours. In this way, corrections for radioactive decay and possible errors introduced thereby from uncertainties in the decay constant of the radioisotope were kept to a minimum.

Estimation of Radioactive Content of Resin

The precise direct experimental determination of the radioactive content of the resin presented many difficulties. Perhaps the most serious was the entrainment of relatively large volumes of the supernatant solution, which could not be removed completely without disturbing the chemical equilibrium between the resin and the solution. Further, it was desirable to count all samples in precisely the same way, in order to permit cancellation of the geometry factor c in Equations (5) and (6). This would require that the resin be converted completely to a water-soluble form containing the same amount of solids as the supernatant solution. While none of these problems are perhaps insurmount-

able, it appeared more feasible to avoid them altogether by estimation of the radioactivity on the resin by difference.

For such a procedure to be reliable, it is necessary to take account of the preferential uptake of water by the resin during equilibration (1). This was done by measurement of the concentration of the major electrolyte BCl in solution before and after equilibration with the resin. The proportion of water taken up by the resin was never very large, e.g., varying from less than 0.1% of the total weight of the solution to not more than 4.9% for the case where the largest weight of resin (2.0 gm.) and smallest weight of solution (11.0 gm.) were used.

Two further steps were taken to ensure the reliability of this method for the estimation of the radioactivity on the resin by difference. (i) The ratio of weight of resin to weight of solution was so chosen that approximately one-half of the radioactivity was on the resin at equilibrium. In this way, the inherently inaccurate estimation of small differences was avoided. In the same way, possible errors were minimized arising from the slight solubility of the resin in water. Marinsky (11) suggests that as much as 0.1% of the resin at equilibrium may be in colloidal solution. If a large fraction of the added tracer were on the resin at equilibrium, the effect of this slight solubility would contribute a disproportionately large error to the estimation of the radioactive content of the supernatant solution. (ii) It was established that adsorption of the tracers on the glass was negligible for all conditions used in the present investigation.

EXPERIMENTAL RESULTS

The equilibrium data for the six systems are given in Tables I to VI. Before commenting on any of these results individually, the general features of these tables will be described. Column 2 in each table gives the molality, at equilibrium, of the electrolyte present in macroconcentration. In Column 3 are given the corresponding molalities of the trace electrolyte. These values were calculated from the amount of radiotracer added, taking account of its absorption on the resin. Column 4 gives the mole ratio of the two components on the resin at equilibrium. These results were calculated from the weight and capacity of the resin used, and the extent of exchange with the radiotracer. They represent the extent of displacement by the tracer of the cation originally on the resin. The tables show that for any given series of experiments, this ratio was maintained low and essentially constant, thus satisfying the requirements of the method. Column 5 gives the distribution of the radiotracer between the resin and solution, in terms of the ratio of c.p.m. per gram of resin to the c.p.m. per gram of solution. In the last column are listed the values of the activity coefficient of the electrolyte present at low concentration. These values were calculated from the experimental results by Equation (10). The values required in these calculations for the activity coefficients of the pure solution of electrolyte BCl were interpolated from a recent compilation (12). Values for the density of the aqueous solutions were obtained from the International Critical Tables.

TABLE I

EQUILIBRIUM DATA FOR THE SYSTEM HYDROCHLORIC ACID – SODIUM CHLORIDE – RESIN

Expt. No.	HCl, m	NaCl, $m \times 10^5$	$\frac{NaR}{HR} \times 10^2$	$\frac{d^*}{e}$	γ_0NaCl
8	0.00502	1.84	0.66**	1457	....
8a	0.00502	0.183	0.066	1470	....
6	0.2016	3.68	0.033	36.2	0.760
7	0.4107	3.70	0.016	17.45	0.739
15	0.6097	24.3	0.068	11.64	0.741
12	0.8544	33.3	0.067	8.44	0.768
17	1.065	40.1	0.061	6.50	0.778
13	1.259	46.3	0.060	5.59	0.812
14	1.562	57.6	0.057	4.33	0.845
5	1.661	7.11	0.007	4.09	0.864

* $\frac{d}{e} = \frac{\text{c.p.m. per gram of resin}}{\text{c.p.m. per gram of solution}}$.

** *Average of four values.*

TABLE II

EQUILIBRIUM DATA FOR SYSTEM HYDROCHLORIC ACID – POTASSIUM CHLORIDE – RESIN

Expt. No.	HCl, m	KCl, $m \times 10^5$	$\frac{KR}{HR} \times 10^2$	$\frac{d^*}{e}$	γ_0KCl
1	0.00502	0.227	0.29	5276	....
2	0.1050	1.31	0.077	238.0	0.771
2a	0.1050	15.1	0.87	235.5	0.767
4	0.1963	3.78	0.12	125.0	0.737
3	0.4080	19.9	0.28	58.1	0.709
5	0.6881	12.5	0.091	32.6	0.700
6	0.9800	19.5	0.10	22.6	0.715
7	1.290	23.7	0.092	16.1	0.742
8	1.573	29.8	0.090	12.6	0.765

* *See footnote*, Table I.*

TABLE III

EQUILIBRIUM DATA FOR THE SYSTEM HYDROCHLORIC ACID – RUBIDIUM CHLORIDE – RESIN

Expt. No.	HCl, m	RbCl, $m \times 10^5$	$\frac{RbR}{HR} \times 10^2$	$\frac{d^*}{e}$	γ_0RbCl
2	0.0100	0.48	0.39	3449**	....
1	0.2141	0.57	0.023	160	0.759
3	0.4215	1.2	0.022	76.7	0.725
4	0.6131	2.5	0.029	49.5	0.709
5	0.8112	2.5	0.021	35.6	0.707
6	1.027	3.0	0.020	27.1	0.717
7	1.235	3.8	0.019	20.9	0.717
7a	1.235	27.0	0.13	21.0	0.717
8	1.507	4.2	0.017	16.8	0.748

* *See footnote*, Table I.*

** *Average of four values.*

TABLE IV

EQUILIBRIUM DATA FOR THE SYSTEM CESIUM CHLORIDE – HYDROCHLORIC ACID – RESIN

Expt. No.	HCl, m	CsCl, $m \times 10^5$	$\frac{\text{CsR}}{\text{HR}} \times 10^2$	$\frac{d^*}{e}$	γ_0CsCl
2	0.01017	0.25	0.30	4850**	....
1	0.1014	0.35	0.041	478	0.788
3	0.2000	1.0	0.024	230	0.740
3a	0.2000	13.0	0.313	232	0.743
10	0.4089	1.0	0.026	104	0.697
9	0.6120	3.4	0.026	66.6	0.687
8	0.8100	4.8	0.025	47.0	0.679
5	1.007	5.8	0.025	36.0	0.681
7	1.267	6.6	0.022	25.9	0.679
6	1.515	8.4	0.022	20.9	0.699

* *See footnote*, Table I.*
** *Average of six values.*

TABLE V

EQUILIBRIUM DATA FOR THE SYSTEM LITHIUM CHLORIDE – SODIUM CHLORIDE – RESIN

Expt. No.	LiCl, m	NaCl, $m \times 10^5$	$\frac{\text{NaR}}{\text{LiR}} \times 10^2$	$\frac{d^*}{e}$	γ_0NaCl
1	0.00504	1.5	0.70	1795	....
5	0.1061	12.1	0.21	79.2	0.756
2	0.3383	12.3	0.076	24.9	0.711
2a	0.3391	123	0.76	25.0	0.711
3	0.672	30.9	0.090	12.4	0.706
4	0.995	42.4	0.083	8.17	0.718
6	1.315	42.1	0.061	6.10	0.742
7	1.653	67.4	0.075	4.75	0.775

* *See footnote*, Table I.*

TABLE VI

EQUILIBRIUM DATA FOR THE SYSTEM POTASSIUM CHLORIDE – SODIUM CHLORIDE – RESIN

Expt. No.	KCl, m	NaCl, $m \times 10^5$	$\frac{\text{NaR}}{\text{KR}} \times 10^2$	$\frac{d^*}{e}$	γ_0NaCl
1	0.00519	0.48	0.063	514	....
1a	0.00519	4.8	0.63	512	....
2	0.2554	33.7	0.093	11.1	0.717
3	0.5203	75.0	0.105	5.71	0.670
4	0.7940	109	0.098	3.75	0.635
5	1.061	143	0.098	2.91	0.622
6	1.401	189	0.097	2.22	0.601

* *See footnote*, Table I.*

The first result in each table gives the average value of two or more determinations of the ratio d/e at the lowest concentration of the major component. In Equation (10) this value is unprimed to distinguish it from the corresponding quantities for higher concentrations. Every other value of d/e in these tables is the average of duplicate experiments.

Pairs of experiments were made at constant concentration of the major component and have been listed, for example, as 8 and 8a in Table I, or 2 and 2a in Table II. These experiments were made to investigate the effect of a 10-fold variation of the mole ratio MR/BR in the resin phase. In every case, such variations produced no differences in the values of d/e greater than the experimental errors in the measurements. It was concluded from this result that the ratio of the activity coefficients of the components in the resin phase remained constant for all experiments in each series, i.e., the parameter g referred to earlier did not vary.

The reproducibility of the measurements was $\pm$ 0.5% when Na^{24} was used, and $\pm$ 0.6–0.7% for the other tracers. The derived values of the activity coefficients of the salts were generally precise to $\pm$0.004–0.005, except for cesium chloride, where the uncertainty is $\pm$ 0.01. The larger error in this case arises mainly from an unusual spread among the six separate results listed as Experiment 2 in Table IV.

The experimental results given in Tables I to VI are shown graphically in Figs. 1 to 6, where in each figure the activity coefficient of the electrolyte MCl at essentially zero concentration is plotted against the molality of electrolyte BCl. Vertical bars on each point indicate the spread in duplicate experiments. The activity coefficients of pure solutions of the electrolytes MCl and BCl are given on each figure for comparison. The significance of the curves marked "theory" in Figs. 1 to 4 is given below.

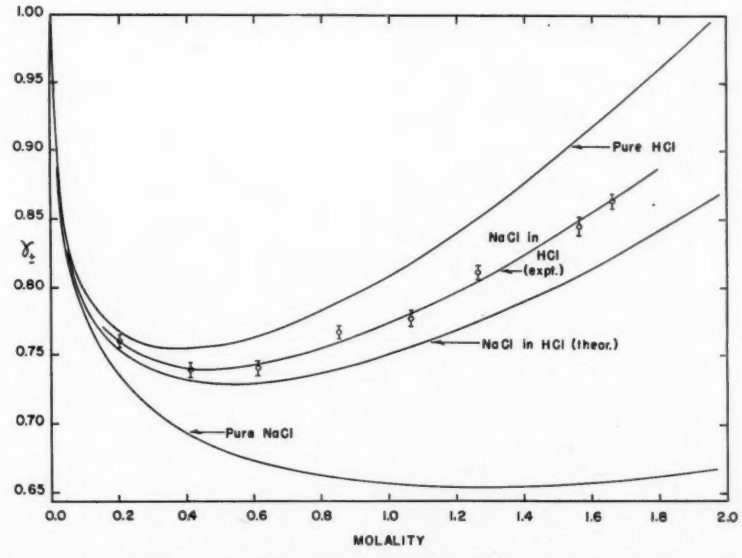

FIG. 1. Theoretical and experimental values of the activity coefficient of sodium chloride at zero concentration in the presence of hydrochloric acid.

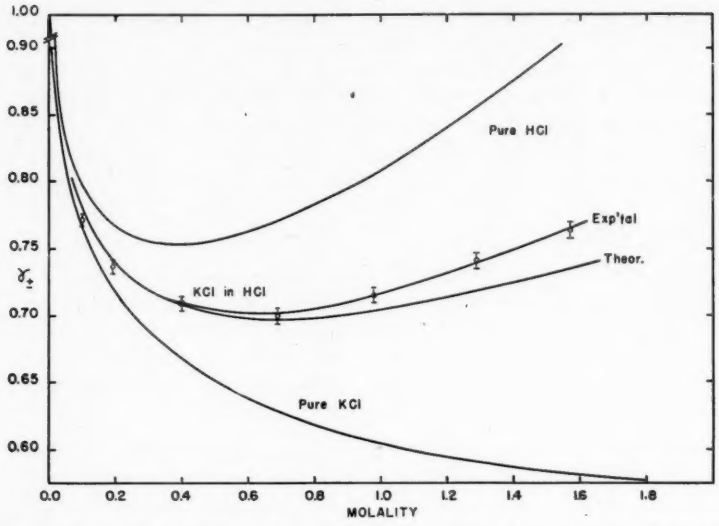

FIG. 2. Theoretical and experimental values of the activity coefficient of potassium chloride at zero concentration in the presence of hydrochloric acid.

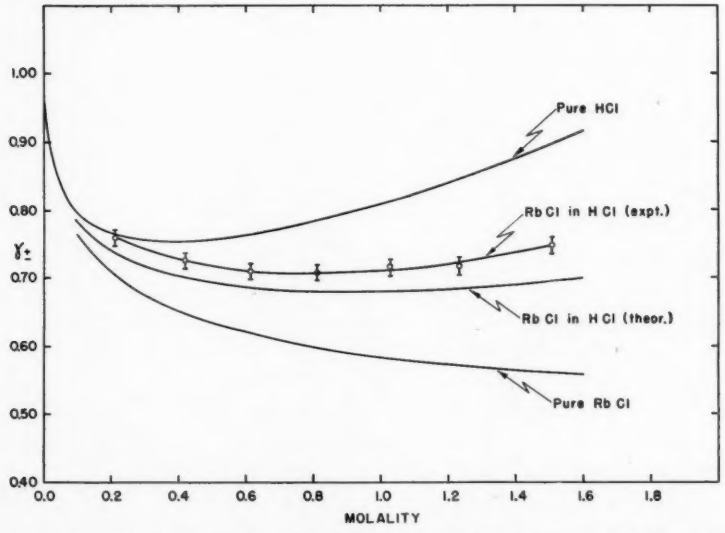

FIG. 3. Theoretical and experimental values of the activity coefficient of rubidium chloride at zero concentration in the presence of hydrochloric acid.

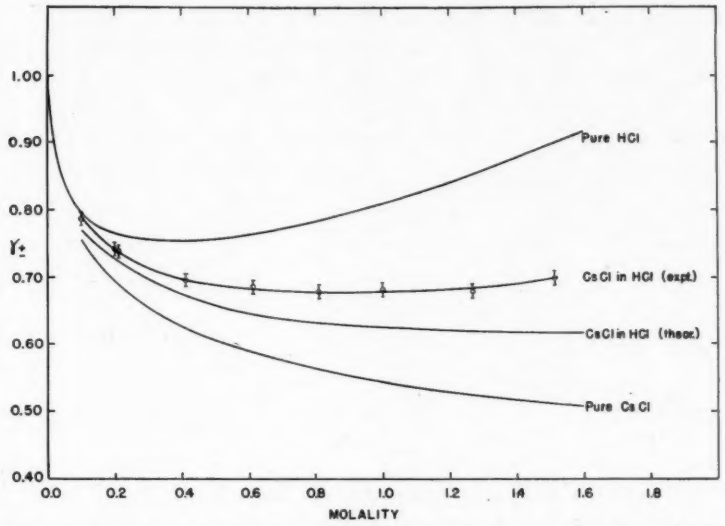

FIG. 4. Theoretical and experimental values of the activity coefficient of cesium chloride at zero concentration in the presence of hydrochloric acid.

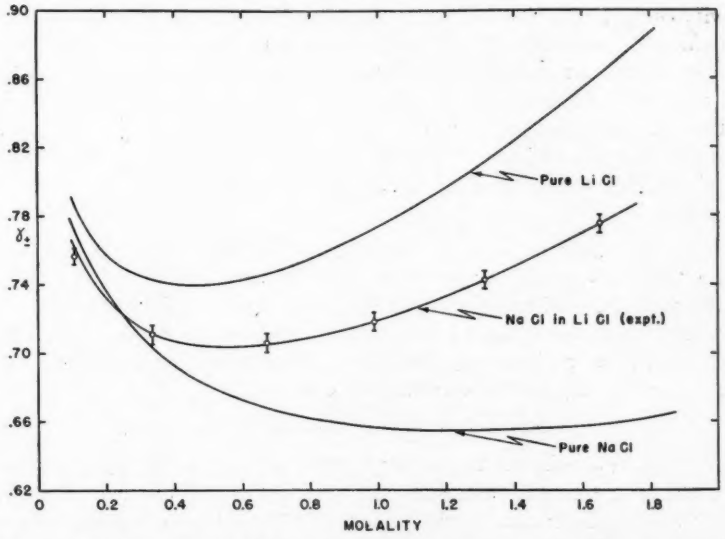

FIG. 5. Experimental values of the activity coefficient of sodium chloride at zero concentration in the presence of lithium chloride.

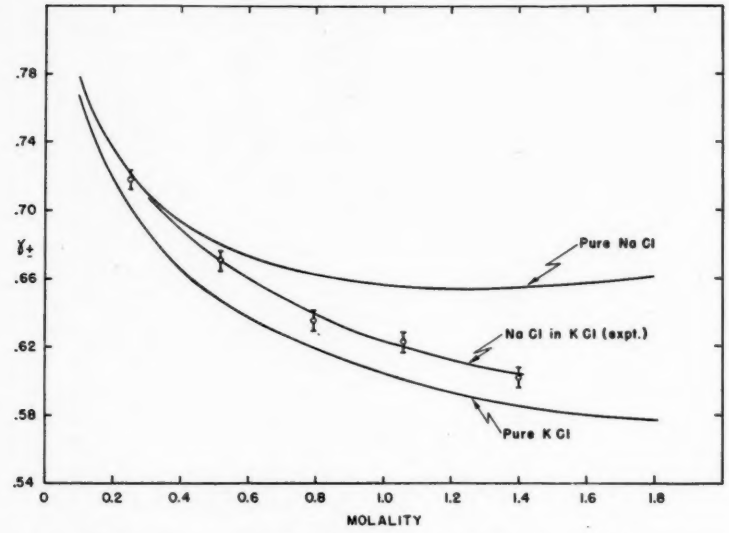

FIG. 6. Experimental values of the activity coefficient of sodium chloride at zero concentration in the presence of potassium chloride.

DISCUSSION

The general features of the results are in qualitative agreement with other studies of mixed electrolytic solutions, in that at a given ionic strength, the activity coefficient of one species lies between those of pure solutions of the two components (8, p.452). Also, it will be noted that the activity coefficient of sodium chloride, at a given ionic strength, is greatest in hydrochloric acid, less in lithium chloride, and least in potassium chloride. This behavior conforms to that for strong acids in mixed electrolytic solution, where it has been observed that the activity coefficient of the acid is greater in the solution of the electrolyte which possesses the higher activity coefficient in the pure solvent (8, p. 453).

To consider the results more quantitatively in terms of the Harned rule, it is necessary to summarize briefly the relevant work on the subject of mixed electrolytes. Several investigations (8, p.459) have shown that the activity coefficient γ, of hydrochloric acid at molality m_1, in the presence of an added alkali chloride at molality m_2, varies at constant ionic strength ($m_1 + m_2 =$ constant) according to the empirical relation:

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_1 m_2 = \log \gamma_{0(1)} + \alpha_1 m_1. \tag{11}$$

The symbol $\gamma_{1(0)}$ refers to the activity coefficient of pure hydrochloric acid at the same ionic strength, and $\gamma_{0(1)}$ to the activity coefficient of hydrochloric acid at zero concentration in the presence of the co-solute, again at the same ionic strength. The quantity α_1 is an empirically determined constant (referred to as α_{12} by Harned). Fig. 7 illustrates how this parameter depends on the

ionic strength of the solution and on the nature of the co-solute. This figure has been constructed from data in the literature (8, p. 467; 12).

Harned (8, p.459) has suggested that similar rules will describe the behavior of the activity coefficient of the alkali chloride in these solutions:

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_2 m_1 = \log \gamma_{0(2)} + \alpha_2 m_2. \tag{12}$$

The symbols have the same meaning as before, except that α_2 is a new constant.

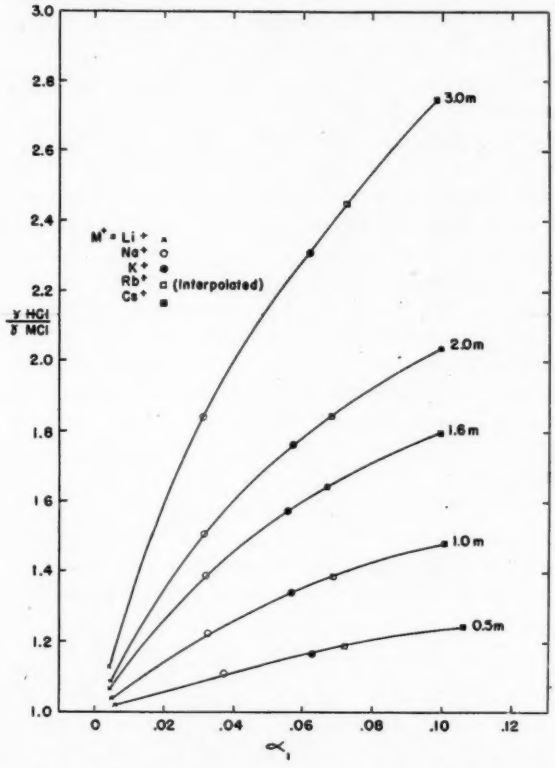

FIG. 7. Variation of the parameter α_1 (Equation 11 in text) as a function of nature and concentration of co-solute.

(This constant is designated as α_{21} in the work already cited (8, p. 459).) If the validity of Equation (12) is assumed, then it is possible by exact thermodynamic methods to calculate the value of α_2 in terms of α_1 and the osmotic coefficients of each of the two solutes in pure solution (8, p.462). Thus:

$$\alpha_2 = \alpha_1 + \frac{2}{2.303m} (\phi_{2(0)} - \phi_{1(0)}) , \tag{13}$$

where $\phi_{2(0)}$ and $\phi_{1(0)}$ are the osmotic coefficients of the salt and acid respectively, in pure solvent at molality m. Values of α_2 calculated from Equation (13) are

probably precise to ± 0.005, corresponding to an uncertainty of ± 0.001 in a_1, and ± 0.2% in the osmotic coefficients.

In order to apply Equations (12) and (13) to the present studies, it is necessary to know the appropriate values of a_1, ϕ_1, and ϕ_2 for the various systems. The osmotic coefficients have been tabulated recently for all the alkali chlorides and for hydrochloric acid (12), and values of a_1 are known for all the alkali chloride – hydrochloric acid systems except rubidium (8, p. 467). Values of a_1 for this latter system can be interpolated with some confidence from Fig. 7; these interpolations are shown on the figure.

The results of such calculations using Equations (12) and (13) are given in Figs. 1 to 4, and are marked "theoretical".

Allowing for the uncertainties in the "theoretical" curves themselves, arising mainly from a ± 0.005 error in the values of a_2, we conclude that the Harned rule is adequate to account for the behavior of potassium chloride, and probably for sodium chloride as well. For the other two electrolytes, the divergences are larger than can be accounted for either from uncertainties in a_2 or in the experimental errors in the present study. The activity coefficients of both rubidium and cesium chlorides in hydrochloric acid are notably higher than the predicted values, the maximum deviation for cesium being about 13%. It should be pointed out that the present comparisons provide a very stringent test of the Harned rule, since the largest extrapolation possible is made in the application of Equation (12).

We now consider the results in terms of the so-called hydration theory of Stokes and Robinson (17). These authors have proposed a two-parameter equation for the activity coefficient of single electrolytes in pure aqueous solution. It is based on the Debye–Hückel theory, and in addition takes into account solvent–ion interactions on the basis that cations are hydrated, and most anions are not (2). For uni-univalent electrolytes at 25°C., their equation is:

$$(14) \quad \log \gamma = \frac{-.5092\sqrt{\mu}}{1+0.3286\,\mathring{a}\sqrt{\mu}} - \frac{n}{2}\log a_w - \log\,[1 - 0.018\,(n-2)m].$$

The ionic strength in volume units is denoted by μ, $\mathring{a}$ is the closest distance, in Ångstrom units, to which the center of the hydrated cation may approach the center of the anion. The other parameter n is a number introduced to allow for all ion–solvent interactions which are large compared to thermal energies. The activity of water is denoted by a_w, and m is the molality of the electrolyte. Values of the parameters n and $\mathring{a}$ have been listed for a large number of electrolytes (17).

The general application of Equation (14), or indeed of any Debye–Hückel type equation, to the calculation of the activity coefficients of the components in mixed electrolytic solution meets with difficulties which have been discussed by Harned (8, p.449). However, when one component is present in very low concentration in the presence of a second electrolyte at relatively high concentration, it appears to us that Equation (14) may be used in the following

way. We shall identify μ, a_w, and m with the values for the single electrolyte present in major concentration. This of course needs no justification. In addition we shall give the parameter n its value characteristic of the major electrolytic component. On a physical basis, this appears reasonable, since the vast majority of the ion–solvent interactions are those involving this component.

With these assumptions, we have substituted our experimental values for the activity coefficient of the trace electrolytes in hydrochloric acid into

TABLE VII

VALUES OF THE PARAMETER $\mathring{a}$ FOR THE ALKALI CHLORIDES IN HYDROCHLORIC ACID SOLUTION

HCl, m	NaCl, $\mathring{a}$	KCl, $\mathring{a}$	RbCl, $\mathring{a}$	CsCl, $\mathring{a}$
0.2	4.20	3.36	4.15	3.36
0.4	4.18	3.24	3.78	2.99
0.6	3.92	3.06	3.36	2.83
0.8	3.90	2.95	3.05	2.58
1.0	3.80	2.89	2.89	2.37
% Decrease in $\mathring{a}$, 0.2 – 1.0 m	9	14	30	29

Equation (14), and solved for $\mathring{a}$, the distance of closest approach. The results are given in Table VII. We note that in every case, the parameter $\mathring{a}$ calculated in this way decreases with increasing concentrations of hydrochloric acid. Similar calculations were made from the results for the activity coefficient of sodium chloride in solutions of lithium chloride and potassium chloride (Tables V and VI). Between the concentrations 0.2 m and 1.0 m of the major electro-

TABLE VIII

VALUES OF THE PARAMETER $\mathring{a}$ FOR HYDROCHLORIC ACID IN ALKALI CHLORIDE SOLUTIONS

MCl, m	MCl = LiCl, $\mathring{a}$	MCl = NaCl, $\mathring{a}$	MCl = KCl, $\mathring{a}$
0.2	4.63	4.69	4.95
0.4	4.72	5.41	5.46
0.6	4.75	5.76	5.95
0.8	4.82	6.13	6.54
1.0	4.85	6.51	7.08
% increase in $\mathring{a}$, 0.2 – 1.0 m	5	39	43

lyte, $\mathring{a}$ for sodium chloride decreased by 1% in lithium chloride solutions, and 10% in potassium chloride solutions.

The data compiled by Harned (8, p.467) dealing with the activity coefficients of hydrochloric acid in alkali chlorides may be treated in a similar manner. The results for the parameter $\mathring{a}$ for hydrochloric acid at zero concentration in three alkali chlorides are given in Table VIII. Here the reverse behavior is observed, i.e., the parameter $\mathring{a}$ appears to increase with increasing concentration of alkali chloride.

The physical relation between the solvent–ion interactions and the size of the ion suggested by Stokes and Robinson is that the latter increases with increasing hydration of the ion (17). If this idea is accepted, then the results in Tables VII and VIII lead to a picture of competitive hydration of the cations in mixed electrolytic solutions. The magnitude of the interactions of the ions with water, deduced from these results, would decrease in the order H, Li, Na, K, Rb, and Cs. In addition, it would be necessary to assume that the strength of the solvent–ion interaction *per ion* in a pure one-component electrolytic solution decreases with increasing concentration of the electrolyte. Stokes and Robinson suggest that this latter effect does indeed become evident at concentrations for which their two parameter equation begins to break down, although they do not consider that such a postulate is necessary in more dilute solutions of single electrolytes (17).

Further work with other solutions of mixed electrolytes would be of interest, to ascertain how generally this hypothesis of competitive hydration may be applied.

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NOTES

Influence of Temperature on the Intermolecular C^{13} Isotope Effect in the Decarboxylation of Normal Malonic Acid

The C^{13} isotope effect in the decarboxylation of normal malonic acid has been investigated by Lindsay, Bourns, and Thode (3) and by Bigeleisen and Friedman (2). The decarboxylation may be represented by the following equations:

$$\begin{array}{l} C^{12}OOH \\ \diagup \\ C^{12}H_2 \\ \diagdown \\ C^{12}OOH \end{array} \xrightarrow{k_1} C^{12}O_2 + C^{13}H_3C^{12}OOH$$

$$\begin{array}{l} C^{12}OOH \\ \diagup \\ C^{13}H_2 \\ \diagdown \\ C^{12}OOH \end{array} \xrightarrow{k_2} C^{12}O_2 + C^{13}H_3C^{12}OOH$$

$$\begin{array}{l} C^{13}OOH \\ \diagup \\ C^{12}H_2 \\ \diagdown \\ C^{12}OOH \end{array} \begin{array}{l} \xrightarrow{k_3} C^{12}O_2 + C^{13}H_3C^{12}OOH \\ \xrightarrow{k_4} C^{12}O_2 + C^{13}H_3C^{13}OOH \end{array}$$

Two isotope effects have been observed experimentally. The deviation from unity of the rate constant ratio $\frac{k_4}{k_3}$ is a measure of the first or intramolecular effect. This ratio, $\frac{k_4}{k_3} = 1.021 \pm 0.001$, indicates a 2.1% greater probability of rupture of a C^{12}–C^{12} bond than a C^{12}–C^{13} bond within the isotopic species malonic acid–1–C^{13} (2, 3). The second or intermolecular effect is given by either the ratio $\frac{k_1}{2k_3}$ or $\frac{k_1}{k_3+k_4}$. The value for the former ratio was reported by Lindsay, Bourns, and Thode from a single experiment to be 1.046. Bigeleisen and Friedman's value for the same ratio was 1.037 ± 0.002.

A theory based on statistical mechanics and the absolute reaction rate theory has been developed by Bigeleisen (1) to account for these effects. Predications made on the basis of this theory (2) give $\frac{k_4}{k_3} = 1.0198$, a value in excellent agreement with the experimental results found for the intramolecular effect. However, the predicted value for the intermolecular effect is considerably less than the value obtained experimentally. According to the theory the intramolecular isotope effect would be expected to be independent of temperature. This was found to be the case (3). Moreover in the small temperature range 137° – 196°C. one would predict the intermolecular effect to be essent-

ially independent of temperature. This has been investigated and the results are reported here.

Five-gram samples of B. D. H. Certified Chemical malonic acid, 99.6% pure by acidimetric titration, were decarboxylated in a test-tube-like reaction vessel in a thermostatically controlled oil bath. The decomposition products were swept out by a stream of pure nitrogen gas, the acetic acid being removed by a dry ice – acetone trap and the carbon dioxide collected in barium hydroxide solution as barium carbonate. Only the first 1 or 2% of carbon dioxide evolved was collected in each case. The carbon dioxide was recovered by treatment of the barium carbonate with dilute phosphoric acid in a high vacuum system and purified by fractionation between traps cooled in dry ice – acetone and liquid air.

It has previously been shown (3) that if the atom fraction of C^{13} occurring in normal malonic acid is given by a, the ratio $\frac{k_1}{2k_3}$ is given for the case considered by:

$$\frac{k_1}{2k_3} = \frac{a}{1-a}\left[\frac{C^{12}O_2}{C^{13}O_2}\right].$$

Combination of the value obtained for this ratio with that found for $\frac{k_4}{k_3}$ permit the calculation of $\frac{k_1}{k_3+k_4}$.

The C^{13} content of the starting malonic acid, a, was obtained from a mass spectrometric analysis of the carbon dioxide produced when a sample of the acid was completely oxidized by a wet oxidation procedure (4). The ratio $\frac{C^{12}O_2}{C^{13}O_2}$ was obtained from mass spectrometric analysis of the carbon dioxide produced at the start of the decarboxylation. All samples of carbon dioxide were analyzed on a 180° direction focusing mass spectrometer. Details of similar analyses are given elsewhere (3).

The decarboxylation was carried out at four temperatures and the results obtained are shown in Table I.

TABLE I

Run	Temp., °C.	$\frac{C^{12}O_2}{C^{13}O_2}$*	$\frac{k_1}{2k_3}$	$\frac{k_1}{k_3+k_4}$**
3F	137°±0.5°	95.94	1.034	1.023
5F	149°±0.5°	96.58	1.041	1.030
7F	173°±0.5°	95.88	1.034	1.023
8F	196°±0.5°	96.13	1.036	1.025
Mean			1.036±0.003***	1.025±0.003***

*All $C^{12}O_2$ ratios are relative to the $C^{12}O_2$ ratio in a normal malonic acid combustion sample assigned a value of 92.77 i.e. $\frac{1-\alpha}{\alpha} = 92.77$.

**Assuming $\frac{k_4}{k_3} = 1.021$ (3).

***Precision is given in terms of standard deviation.

It is seen that the intermolecular effect remains constant in the temperature range 137 – 196°C., a fact which is in agreement with theoretical predictions. Moreover, the ratio $\frac{k_1}{2k_3} = 1.036 \pm 0.003$ is in closer agreement with the results of Bigeleisen and Friedman ($1.037 \pm .002$) than the value previously reported from this laboratory. Although the magnitude of the effect is not in agreement with the predicted value of 1.021 calculated by Bigeleisen (2), the invariance of the effect with temperature is an interesting partial substantiation of theory.

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The Nitrosation of Hexamine

The aim of this work was to raise the yield of trimethylenetrinitrosamine, the nitroso analogue of RDX, from hexamine. Although it was not attained, the results may have some theoretical interest. Bachmann and Deno (1) have recently referred to part of them.

A number of variations of the original method of Mayer (2) were tried. The basic procedure was to add successively 1 mole equivalent of hexamine, then 4.8 moles sodium nitrite, to 5.5 moles hydrochloric acid, all in water solution near 0°C. With total water 31 cc. per gram hexamine, reaction time 30–60 min. followed by filtration, washing with water at 0°, and drying to constant weight at 50°, these proportions gave a 48–52% yield of trinitrosamine, m.p. 99–100° corr. or better (pure trinitrosamine, m.p. 105–107°). The yield figure is on a mole-for-mole basis. No change in this procedure gave any higher yield. All runs were made with 10.5 gm. (0.075 mole) hexamine and corresponding amounts of the other reagents.

When the reaction stood only 15 min. before working up, the product was a mixture of trinitrosamine and the less degraded dinitrosopentamethylenetetramine (m.p. pure, 207°). The dinitroso compound could be isolated readily because of its lower solubility in boiling 95% ethanol (1 gm. dissolved in about 60 cc. solvent, compared with 8 cc. for trinitrosamine). A mixture was also obtained when the amount of hydrochloric acid was reduced to 4.4 moles; Bachmann and Deno have shown that this is because of a pH effect. Simply allowing the hexamine and acid solutions to stand together for one and one-half hours or more, or allowing the aqueous hexamine solution to stand alone for about 10 days, before reaction, also gave a mixture under conditions where trinitrosamine would otherwise have been the sole product.

Doubling the nitrous acid lowered the yield to 38–40%. No effect was observed when the reaction volume was doubled, or when sodium chloride was added in an effort to salt out more product. Stirring was found to have no effect provided the reagents were once thoroughly blended at the start, by vigorous mixing for about 30 sec.

Carbon lost in the reaction could be largely accounted for as formaldehyde; the procedure used was dimedone precipitation (3). The formaldehyde found corresponded to 61–64% of the carbon originally present in the hexamine. The 48–52% yield (on mole-for-mole basis) of trinitrosamine corresponds to a further 24–26% of the original carbon. Altogether, therefore, the two products contained 85–90% of the carbon from the hexamine.

The formaldehyde found was slightly higher when the filtrate had been allowed to stand a few days first. Probably this was from decomposition of product remaining in the solution.

Nitrogen peroxide (from a commercial cylinder), added either as liquid or gas to hexamine solution, gave yields of trinitrosamine as high as 48% when 8-10 moles per mole hexamine was used. Addition of 2 to 5 moles ammonium hydroxide had no effect in dilute solution (yield was slightly lowered in concentrated solution). When 5 moles sodium hydroxide was added, the product was nearly all the dinitroso compound.

Dinitrosopentamethylenetetramine, when powdered to −200 mesh and treated with 4 moles of nitrous acid at 0–3°, was converted to trinitrosamine, m.p. 105°, in a maximum yield of 40% after 50 min. With 2 moles of nitrous acid the product was a mixture.

A point of interest in the results is that hexamine in water or dilute acid, on standing, gave a solution which would no longer give pure trinitrosamine with nitrous acid as did the fresh reagents. Instead a mixture of the two nitroso compounds was produced. The mechanism for this is still unknown.

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Wheat Straw Native Lignin*

An attempt has been made to isolate native lignin from mature wheat straw (Saunders) by extracting the finely ground material with alcohol at room temperatures and removing the water- and the ether-soluble fractions. A considerably smaller percentage of lignin was obtained in this way than has been reported as isolable from spruce (1) and aspen (2) by Brauns *et al.* and

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from oak, birch, maple, and white Scots pine by Kudzin and Nord (4). The results of a typical experiment are shown in Table I.

TABLE I

ALDEHYDE YIELD FOLLOWING THE NITROBENZENE OXIDATION OF VARIOUS WHEAT STRAW EXTRACTS

	Whole straw, 563 gm.	Total ethanol extract, 13.0 gm.	Water soluble, 6.47 gm.	Ether soluble, 5.90 gm.	Crude native lignin, 0.238 gm.	Partially purified native lignin, 0.050 gm.
% Vanillin	1.95	0.49	0.33	0.38	1.59	1.69
% Syringaldehyde	2.31	0.42	0.26	0.33	2.03	2.35

The 0.238 gm. of crude native lignin obtained from 563 gm. of straw represent a yield of 0.04% compared with 0.7 to 1.5% isolated from various woods by the above workers. Micro alkaline nitrobenzene oxidations of each fraction (5), the results of which are also shown in the above table, indicate that:—

(i) "Lignin" is partially soluble in water and in ether.

(ii) These water- and ether-soluble lignin fractions differ from the "native" lignin fraction and from the lignin remaining in the straw in that they give rise to different ratios of vanillin to syringaldehyde.

(iii) The aldehyde yield from the crude and partially purified native lignins is much lower than the yield from the lignin which remains in the straw. (On the basis of 14% lignin in the straw the aldehyde yield from the unextracted lignin would be 14% vanillin and 16.5% syringaldehyde.)

This difference between the extracted and unextracted lignins is not surprising in view of the finding by Kudzin, DeBaun, and Nord (3) that native lignins from oak and birch do not give rise to syringaldehyde on oxidation whereas the total lignin from these woods gives very good yields. Evidently the lignin which is extractable with cold ethanol is quite often unrepresentative of the total lignin in the plant.

It is probable that the effect mentioned in (ii) is partially due to the presence of lignans. In this connection it was found that free vanillin was present in small amounts in both the water- and ether-soluble fractions.

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Note on the Preparation of Hydrazine by Arc Electrolysis in Liquid Ammonia*

Although recent work by Pleskov (1) indicates the possibility of discharging the amide ion in liquid ammonia, and he speculates that the condensation of amide radicals should lead to hydrazine, no experimental evidence is presented to support the suggestion.

Experiments made in these laboratories with direct current discharges between a platinum electrode and a cathodic surface of liquid ammonia have shown that hydrazine may be recovered in yields up to 0.2% based on ammonia disappearance. The product is pure, and the yield is a linear function of the quantity of electricity consumed in the electrolysis (Fig. 1). If the discharge

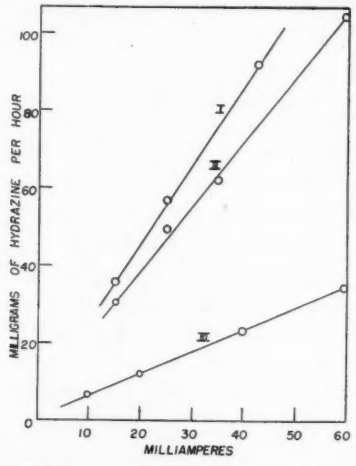

Fig. 1. Rate of hydrazine formation as a function of electrolysis current.
I. Redistilled ammonia, condenser included in power supply.
II. Unpurified cylinder ammonia, condenser included in power supply.
III. Redistilled ammonia, condenser excluded from power supply.

potential is maintained near its peak value of 4000 v. for longer periods by the presence of a 4 μf. condenser in the power rectification circuit, the yields of hydrazine are substantially increased. Since the yields are in excess of those calculated by Faraday's laws for the simple discharge of the amide ion, it is probable that hydrazine is produced by a chain reaction operating in the gaseous discharge above the liquid surface.

1. PLESKOV. Acta Physiochim. U.R.S.S. 20: 578. 1945.

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